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**THE RARE-EARTH ELEMENTS
AND THEIR COMPOUNDS**

The
RARE-EARTH ELEMENTS
and
THEIR COMPOUNDS

By

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To

ROBERT ANDREWS MILLIKAN

*Whose experimental researches in physics have had a
profound effect on our understanding of chemistry.*

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PREFACE

The discovery of most of the rare-earth elements took place in the latter half of the nineteenth century, but the purely chemical methods of study available in that period and the monotonously similar chemical behavior of the members of this group of substances placed them for some time in the category of puzzling but rather dull mysteries. Not only were their nature and an understanding of their place in the periodic system obscure, but also they came to be virtually dismissed in many textbooks, the authors of which designated any and all of these elements as "rare earths," which were to be noted but not further examined.

Following the discovery and precise investigation of electrons, X-rays, and spectral lines, and the introduction of the quantum theory of atomic structure, combined with thermodynamics and statistical mechanics, the interesting magnetic and spectroscopic properties of the rare-earth elements were explained, and the similar chemical behavior of these elements was clarified. Certainly one of the important successes of our present concepts of atomic structure is the knowledge gained of the nature of the rare-earth elements, and it is significant that these concepts were formed as the result of experimental facts that were found in the fields of both physics and chemistry. It is of importance here, as in other branches of science, that discoveries carrying with them a predictive character are the most satisfying to the scientist and most helpful to the engineer.

The purpose of the present monograph is to present the principal chemical and physical properties of the rare-earth elements and their compounds and to exhibit the concordance of the current theories with these properties. As far as is possible, this phase of the treatment is a quantitative one, and the experimental data presented have been selected with some care. Equal emphasis is placed on the descriptive chemical properties such as methods of separation, preparation, reactions, and solubilities, because experimental chemists and physicists depend strongly on them in both purely scientific studies and in practical applications.

Frequent references to original literature sources are given; these references, although not complete, are meant both to be of a significant character and to serve as a key to those who wish to make a more com-

prehensive study of the whole or a part of the chemistry and physics of the rare earths. Since the research point of view is emphasized, instructors who follow the topical method in advanced courses on inorganic chemistry may, on this account, find the monograph useful in their classes. It is assumed that the reader or student is thoroughly familiar with modern physical chemistry and physics.

Because some rare-earth elements occur as products of the fission of thorium and uranium, the published nuclear properties of the rare earths are included in an appendix. A survey of the fission products of uranium was published as recently as November, 1946, in the *Journal of the American Chemical Society*; that brief article presents the results of a monumental accomplishment. We regret that detailed consideration of the subject matter was not possible in this monograph, but we are glad to call attention to it in this preface.

We wish to express here our appreciation for the direct or indirect assistance and the helpful counsel given us by Professors R. M. Badger, R. G. Dickinson, E. H. Swift, R. C. Tolman, and especially by Professor Wendell Latimer. Mr. and Mrs. John B. Hatcher kindly made all the drawings for the figures and graphs, and we are grateful for their care and interest in assuring that both accuracy and good appearance were maintained throughout this aspect of the work. Mrs. Ellen Garner and Mrs. Marguerite S. Yost have given welcome assistance in several phases of the writing and correcting during the last ten years.

One of the authors, Dr. Horace Russell, Jr., a very young man, passed away while working at the Los Alamos laboratory of the Manhattan Project. To him, as an able co-worker and as a close friend, we owe more than can be easily expressed.

DON M. YOST
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February 4, 1947

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Chapter 1

ELECTRONIC STRUCTURES AND OXIDATION STATES OF THE RARE-EARTH ELEMENTS

Occurring between barium (Group II) and hafnium (Group IV) in the periodic table is a group of fifteen * chemically similar elements known as the rare earths. The selection of the term "rare earths" to designate these elements arose from their relative scarcity at the time this name was proposed and from the fact that their oxides resemble the alkaline-earth oxides. Inasmuch as the periodic law predicted but one element between barium and hafnium, the existence of the rare-earth group was for some time a puzzling phenomenon. The development of the theory of atomic systems has shown that the explanation lies in the unusual electronic structures of these atoms.

Electronic Configurations of the Rare Earths.† Unfortunately, the rare earths occupy the region of the periodic table which has been least investigated by spectroscopists. In 1927 Hund, in his book *Linienpektren und periodisches System der Elemente*, could say, "Nur in einer Stelle des periodischen System klappt eine grosse Lücke. Von den seltenen Erden ist noch kein Spectrum in Terme geordnet." This was so not only because of the difficulty of separating and purifying the elements but more especially because of the extreme complexity of some of the spectra; the number of lines experimentally observed seems to depend largely upon the amount of exposure given. This complexity is so great that, for example, a change from one configuration to another in a neutral gadolinium atom can give rise to more than 20,000 lines even if there is adherence to the strictest selection rules; if only the *J* selection rule is retained, more than 18,000,000 lines are possible, whereas the same transition in cesium gives only two lines [Albertson, *Phys. Rev.*, **47**, 370 (1935)].

* Spectroscopists usually do not include lanthanum in the rare-earth group since the complete absence of a 4*f* electron leads to a relatively simple spectrum very different from that of the other elements in the group. Chemists, however, include lanthanum on the basis of its chemical properties. This practice is followed here, and fifteen rare earths are recognized.

† The authors are indebted to Dr. H. N. Russell of the Princeton Observatory for helpful discussions on this topic.

In addition, rare-earth spectra are usually excited by means of an arc or spark, and this excitation produces a high percentage of ions (the first ionization potential ranges from five to seven electron volts). Under these conditions the intensities of the lines due to ions are likely to be much greater than those of the lines due to unionized atoms, and the spectra of the latter are consequently more difficult to observe and measure. This difficulty has been partly met by the use of thermal excitation of the neutral atom. The experimental problem has been elegantly solved by Dr. A. S. King of the Mount Wilson Observatory. He used a graphite furnace heated in vacuum by passing several thousand amperes of current through the tube wall [see *Astrophys. J.*, **56**, 318 (1922), for a description of the furnace]. The substance to be vaporized was put in the center of the tube, and simultaneous observations were made of the spectrum and of the temperature through windows at each end of the heavy, water-cooled case. In such a furnace the temperature may be raised above 3200° C. In this way a temperature classification of the lines is made which helps greatly in the analysis.

A concentrated attack on the problem by Drs. Walter Albertson and G. R. Harrison at the Massachusetts Institute of Technology, W. F. Meggers of the National Bureau of Standards, and H. N. Russell of the Princeton Observatory has resulted in a clarification of the situation. The ground states of seven of the rare earths in the neutral state and of ten in the singly ionized state have been established with considerable certainty. These are presented in Table 1. The elements which immediately precede and follow the group are given also for the sake of comparison.

References to individual papers on the known spectra may be found in articles by W. F. Meggers [*J. Optical Soc. Am.*, **31**, 157 (1941), and *Rev. Modern Phys.*, **14**, 96 (1942)]. The ground states for cerium, praseodymium, and neodymium are predicted by Dr. H. N. Russell on the basis of the recently determined ground states of the singly ionized atoms. These predictions may be made with considerable confidence, but the ground states enclosed in double parentheses are little more than guesses based on the general appearance of the very complex spectra [see Albertson, *Astrophys. J.*, **84**, 26 (1936)]. Element 61 has not been isolated, and its configuration is based purely on an interpolation.

The older view, based on the predictions of Hund, that the neutral rare earths had the normal electronic configuration $4f^n 5d6s^2$, where n goes from 0 to 14, is seen to be incorrect in many cases. Indeed the more general rule is for the rare-earth atoms to have no electron in a

TABLE 1

GROUND STATES OF THE NEUTRAL AND SINGLY IONIZED RARE-EARTH ELEMENTS¹

Element	Symbol	Atomic No.	Neutral Atom		Ionized Atom, M ⁺
			Configuration ²	Term Symbol	Configura- tion ² and Term Symbol
{ Cesium	Cs	55	0 2 6 0 1	² S _½	¹ S ₀
{ Barium	Ba	56	0 2 6 0 2	¹ S ₀	² S _½
Lanthanum	La	57	0 2 6 1 2	² D _½	5d ² ³ F ₂
Cerium	Ce	58	(2 2 6 0 2	³ H)	4f ² 6s ⁴ H _½
Praseodymium	Pr	59	(3 2 6 0 2	⁴ I)	4f ³ 6s ⁵ I ^o ₄
Neodymium	Nd	60	(4 2 6 0 2	⁵ I)	4f ⁴ 6s ⁶ I _½
Element 61		61	((5 2 6 0 2	⁶ H))	
Samarium	Sm, Sa	62	6 2 6 0 2	⁷ F ₀	4f ⁶ 6s ⁸ F _½
Europium	Eu	63	7 2 6 0 2	⁸ S ^o _½	4f ⁷ 6s ⁹ S ^o ₄
Gadolinium	Gd	64	7 2 6 1 2	⁹ D ^o ₂	4f ⁷ 5d6s ¹⁰ D ^o _½
Terbium	Tb	65	((8 2 6 1 2	⁸ H))	
Dysprosium	Dy	66	((10 2 6 0 2	⁵ I))	
Holmium	Ho	67	((11 2 6 0 2	⁴ I))	
Erbium	Er	68	((12 2 6 0 2	³ H))	
Thulium	Tm, Tu	69	13 2 6 0 2	² F ^o _½	4f ¹³ 6s ³ F ^o ₄
Ytterbium	Yb	70	14 2 6 0 2	¹ S ₀	4f ¹⁴ 6s ² S _½
Lutecium	Lu	71	14 2 6 1 2	² D _½	4f ¹⁴ 6s ² ¹ S ₀
or cassiopeium	Cp				
{ Hafnium	Hf	72	14 2 6 2 2	³ F ₂	
{ Tantalum	Ta	73	14 2 6 3 2	⁴ F _½	

¹ Meggers [*Rev. Mod. Phys.*, **14**, 96 (1942)] has published a recent, comparatively detailed review and analysis of the spectroscopic data for the rare-earth elements. His term assignments differ in some respects from those shown in Table 1.

² The inner shells are completely filled and are not shown.

5d orbital in the ground state. It should be noted that gadolinium, which has the predicted configuration, contains a half-completed subshell. The stability of this half-completed subshell plays an important part in the interpretation of the observed valences of the group. The deviations from the expected 4fⁿ5d6s² configurations are not greatly surprising as the systems are so complex that no definite predictions based on fundamental theory can be made. The general conclusions

of chemical interest as to the nature of the rare-earth group are not altered. As was formerly known, the marked similarity in chemical behavior results from the existence of the seven $4f$ states with a capacity for fourteen electrons. The nature of the resulting energy levels is such that three electrons are removed comparatively easily to give the normal trivalent state. The $4f$ electrons are not involved in the formation of chemical bonds, and the electrons remaining in these states are perturbed only slightly by the fields due to neighboring atoms. Thus the $4f$ electrons exert only a secondary influence on the chemical properties, although they give rise to the color and paramagnetism characteristic of many elements of the group.

Oxidation States of the Rare Earths. The normal oxidation state common to all the rare earths is the tripositive state. In this state three electrons are removed from the neutral atom, leaving the configuration $4f^n$, where n goes from 0 to 14. This configuration would be expected for the tripositive ion regardless of which configuration, $4f^n 5d 6s^2$ or $4f^{n+1} 6s^2$, is the ground state of the neutral atom. The spectroscopic determinations of the ground states do not then affect calculations previously made for the ions. The correctness of the configuration $4f^n$ is indeed confirmed by the excellent agreement between the observed and calculated magnetic susceptibilities and, in the case of Ce^{+++} with the ground state $4f^2 F_{3/2}$, by spectroscopic analysis [Lang, *Phys. Rev.*, **49**, 552 (1936)].

It has been known for some time that an oxidation state other than +3 is possible for many rare earths. These so-called "anomalous" valences are best approached and most easily remembered through a consideration of their electronic structure. Three configurations among the rare-earth ions are especially stable. The first and most stable is that of La^{+++} , which has the configuration of xenon, an inert gas with a 1S ground state. The second is that of Gd^{+++} , which has the $4f$ shell half completed ($4f^7$). By Hund's rule * this arrangement has the maximum multiplicity possible ($2S + 1 = 8$) and must consequently be an S state ($L = 0$) through the Pauli exclusion principle. Both

* The rules for the determination of the lowest-lying term for a given configuration, known as Hund's rules, are as follows: 1. (a) Of all the terms allowed by the Pauli principle, that one with the maximum multiplicity lies lowest (multiplicity $= 2S + 1$, where S is the resultant spin quantum number). (b) If several terms have the maximum multiplicity, that term with the greatest L lies lowest (L = resultant electronic orbital momentum quantum number). These rules have been found to hold for the lowest-lying term, i.e., the normal state, in all atoms and ions, although many deviations are found in excited states. A further useful rule is:

2. Multiplets arising from a configuration consisting of less than half the electrons in a completed subgroup are usually normal (smallest J lowest) and those

TABLE 2

CONFIGURATIONS OF THE RARE-EARTH IONS AND THE OBSERVED OXIDATION STATES

Element	Atomic No.	M ⁺⁺	M ⁺⁺⁺	M ⁺⁺⁺⁺	M ⁺⁺⁺⁺⁺	Observed Oxidation States ¹
La	57		Xe configuration			+3
Ce	58		<i>f</i>	Xe configuration		+3, 4
Pr	59		<i>f</i> ²	<i>f</i>	Xe configuration	+3, 4 or +5
Nd	60		<i>f</i> ³	<i>f</i> ²		+3, 4(?)
61	61		<i>f</i> ⁴		
Sm	62	<i>f</i> ⁶	<i>f</i> ⁵			+2, 3
Eu	63	<i>f</i> ⁷	<i>f</i> ⁶			+2, 3
Gd	64		<i>f</i> ⁷			+3
Tb	65		<i>f</i> ⁸	<i>f</i> ⁷		+3, 4
Dy	66		<i>f</i> ⁹			+3
Ho	67		<i>f</i> ¹⁰			+3
Er	68		<i>f</i> ¹¹			+3
Tm	69		<i>f</i> ¹²			+3
Yb	70	<i>f</i> ¹⁴	<i>f</i> ¹³			+2, 3
Lu	71		<i>f</i> ¹⁴			+3

¹ In addition an oxidation state of +2 has been reported for La, Ce, Pr, Nd, Gd, and Tm. See text.

observation and quantum-mechanical calculations show a half-completed subshell to be especially stable. This stability is illustrated in the neutral atoms by the fact that both europium and gadolinium have seven 4*f* electrons. Other examples are found in other places in the periodic table, as in the sequence neutral vanadium with the configuration 3*d*³4*s*², chromium with 3*d*⁵4*s* (instead of 3*d*⁴4*s*²), and manganese with 3*d*⁵4*s*².

from a configuration consisting of more than half are usually inverted (largest *J* lowest). (Multiplets are terms formed through the various combinations of a given *S* and *L* and are characterized by the quantum number *J*, *J* being the vector sum of *S* and *L*.)

In standard spectroscopic notation the value of *L* is represented by a capital letter (*S*, *P*, *D*, *F*, *G*, *H*, *I*, *K* = 0, 1, 2, 3, ...); the multiplicity, (2*S* + 1), is given by a superscript on the left, and the *J* value by a subscript on the right. If the arithmetic sum of the *l*'s for the individual electrons is odd, an *o* is added as a superscript on the right-hand side. An examination of Table 1 for the rare earths will show that the rules given above are followed.

The third stable electronic arrangement is that of Lu^{+++} , which has only completed subshells and is consequently also in an 1S state. Neutral ytterbium shows this stability by its ground state $4f^{14}6s^2\ ^1S$ instead of $4f^{13}5d6s^2\ ^3H_6$.

Since these three states are especially stable, one might expect to find ions with these configurations, and these expectations are realized. Table 2 gives the configurations for the various ions with the more important isoelectronic sequences connected by arrows. The known chemical oxidation states are listed for each element. A reasonable explanation is provided for the stability of dipositive europium and ytterbium and of tetrapositive cerium and terbium. Samarium would be expected to have a less stable dipositive state than europium. There would seem to be a good chance to find dipositive thulium, although its stability would certainly be less than that of dipositive ytterbium. Praseodymium is the most likely of the elements to have an oxidation state of +5. Maximum chemical ionizations fixed by the configurations are three for lanthanum, lutecium, and probably gadolinium, four for cerium, and five for praseodymium. However, the table can tell little about the possibility of existence of dipositive states for most of the elements.

Consideration of such a table has been of much help in working with the rare earths. W. Klemm, who recognized clearly its value, was able to predict and then prepare dipositive ytterbium [*Z. anorg. allgem. Chem.*, **184**, 345 (1929)]. Workers in his laboratory have shown that some physical properties such as molar volumes (Fig. 1) show a slight break at gadolinium in the gradual change from element to element [Bommer, *Z. anorg. allgem. Chem.*, **241**, 273 (1939)]. The observed variations in properties among the rare-earth group have led to many attempts to spread the elements across the periodic table in various ways [Brauner and Švagr, *Collection Czechoslov. Chem. Commun.*, **4**, 49, 244 (1932); Yagoda, *J. Am. Chem. Soc.*, **57**, 2329 (1935)]. Although there is a certain periodicity of properties, there seems to be no justification for forcing the elements into other columns of the periodic table.

The evidence for the doubtful chemical valences shown in Table 2 will be discussed here; more detailed information about the well-known compounds will be found in Chapter 6. The highest oxidation state of a rare earth which may be said to be fairly well supported is +5 for praseodymium. A hexapositive valence has indeed been suggested for cerium in a compound obtained by the action of hydrogen peroxide on cerous nitrate in ammoniacal solution. A dark red precipitate results, having the composition $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$ [Schwarze and Geise, *Z. anorg.*

allgem. Chem., **176**, 209 (1928)]. However, the compound reduces permanganate in acid solution, and later work has shown that it is a peroxide of tetrapositive cerium and does not contain hexapositive cerium.

The valence of 5 for praseodymium is more firmly, although by no means conclusively, established. Several investigations have shown that higher oxides are formed when the sesquioxide is ignited in air [Prandtl

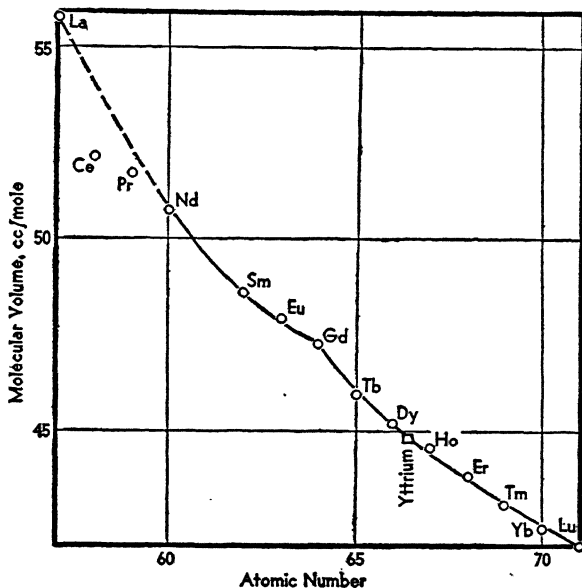


FIG. 1. Molecular volumes of the rare-earth elements.

and Huttner, *Z. anorg. allgem. Chem.*, **149**, 235 (1925); Pagel and Brington, *J. Am. Chem. Soc.*, **51**, 42 (1929); Jantsch and Weisenberger, *Monatsh.*, **60**, 1 (1932); Marsh, *J. Chem. Soc.*, **1946**, 15]. It is generally agreed that the black ignition product can be represented by the empirical formula Pr_6O_{11} , which may be considered to be $\text{Pr}_2\text{O}_5 \cdot 2\text{Pr}_2\text{O}_3$, i.e., a praseodymium praseodymate. The best evidence for this formula comes from Prandtl and Rieder [*Z. anorg. allgem. Chem.*, **238**, 225 (1938)], who heated mixtures of the sesquioxides of yttrium and praseodymium in oxygen under different conditions and determined, by weighing the resulting product and then reducing it by hydrogen and weighing again, how much oxygen was taken up. Their results are presented in Table 3. Since yttrium is known only in the tripositive state, the data indicate that under the most favorable conditions a con-

TABLE 3
ABSORPTION OF OXYGEN BY Pr_2O_3 AND Tb_2O_3 WHEN MIXED WITH Y_2O_3
AND HEATED

Oxide Mixture, Moles $\text{Pr}_2\text{O}_3 + \text{Y}_2\text{O}_3$	Atomic Weights of Oxygen Taken up per Mole of Pr_2O_3		
	Heated in Air	Heated in O_2 at 350°C	
		1 atm	15 atm
1 + 0	0.65	0.78	1.07
1 + 1	0.77	0.94	1.16
1 + 4	1.03	1.09	1.62
1 + 7	1.11	1.61	1.71
1 + 9	1.03	1.41	1.80

Ratio O to Pr_2O_3 : $\frac{\text{Pr}_6\text{O}_{11}}{0.67}$ $\frac{\text{PrO}_2}{1.00}$ $\frac{\text{Pr}_2\text{O}_5}{2.00}$

Oxide Mixture, Moles $\text{Tb}_2\text{O}_3 + \text{Y}_2\text{O}_3$	Atomic Weights of Oxygen Taken up per Mole of Tb_2O_3				
	Heated in Air	Heated in Oxygen			
		1 atm 350°C	6 atm 350°C	20 atm 300°C	30 atm 330°C
1 + 1	0.45	0.78	0.84	0.78	0.87
1 + 3	0.23	0.62	0.91	0.85	0.93
1 + 5	0.09	0.43	0.87	0.83	0.98

Ratio O to Tb_2O_3 : $\frac{\text{Tb}_4\text{O}_7}{0.50}$ $\frac{\text{Tb}_6\text{O}_{11}}{0.67}$ $\frac{\text{TbO}_2}{1.00}$

siderable percentage of the praseodymium is in the form of a praseodymate.

Recently, Marsh (*loc. cit.*) has repeated the work of Prandtl and Rieder and obtained evidence for the formation of PrO_2 , but none for the existence of pentapositive praseodymium. It would be of great interest to test this by magnetic susceptibility measurements. An

unambiguous answer should be obtained as $\mu(\text{Pr}^{4+}) = 2.56$, and $\mu(\text{Pr}^{5+}) = 0$ Bohr magnetons. Presumably under some conditions tetrapositive praseodymium is formed. However, since Pr^{5+} has the xenon configuration, an extremely stable arrangement, it may be that Pr^{5+} is more stable than Pr^{4+} , and Prandtl favors this view. By heating praseodymium sesquioxide, Pr_2O_3 , in oxygen under pressure or with sodium chlorate a black oxide with the formula PrO_2 is obtained (see the references above).

Crystal structure studies by Goldschmidt and by Scherrer and Palacios using the powder method (*Strukturbericht*, 1, 198; 2, 259) have indicated that the substance is a definite compound with a structure of the fluorite type as is that of the well-known CeO_2 . Goldschmidt's data suggest an ionic radius for praseodymium supporting an oxidation number of +4 rather than +5. Since the conclusions are based on X-ray powder photographs alone, they are open to some question. It is possible that some closely similar structure containing praseodymium in two valence states would also explain the observed X-ray pattern. Magnetic measurements by Klemm [*Z. angew. Chem.*, 44, 254 (1931)] are said to support the view that the praseodymium is tetrapositive, but the magnetic method cannot distinguish between tetrapositive praseodymium and a mixture of +3 and +5 praseodymium. The question of the oxidation states in the oxides may not be regarded as settled. Detailed crystal structures would probably be decisive. No higher oxidation states of praseodymium (or terbium) are known in solution. Oxygen is liberated from the higher oxides on treatment with a non-reducing acid. Praseodymium dioxide reacts with hydrochloric acid forming chlorine, liberates iodine from hydriodic acid, oxidizes manganous to manganic ion, cerous to ceric sulfate, stannous to stannic chloride, and ferrous to ferric ion. The tripositive-tetrapositive praseodymium formal potential has been estimated to be more negative than -1.6 volts (Latimer, *Oxidation Potentials*, Prentice-Hall, 1938).

Identical treatment of mixtures of terbium and yttrium sesquioxides gave significantly different results, as seen from Table 3. Here the highest oxygen absorption corresponds to formation of $\text{Y}_2\text{Tb}_2\text{O}_7$ with terbium tetrapositive. It was also confirmed, as had been previously reported, that on glowing Tb_2O_3 in air a dark brown oxide of the approximate formula Tb_4O_7 is formed. This would presumably be $2\text{TbO}_2 \cdot \text{Tb}_2\text{O}_3$. This oxide is unstable at higher temperatures and is decomposed entirely into the colorless sesquioxide on heating at 800°C in nitrogen. It is easily reduced by heating in a stream of hydrogen. The higher oxide of praseodymium is less easily reduced by hydrogen or decomposed by heating.

Similarly, higher oxides of neodymium have been described in the literature [Brauner, *Collection Czechoslov. Chem. Commun.*, **5**, 279 (1933); Marc, *Ber.*, **35**, 2382 (1902); Meyer and Koss, *Ber.*, **35**, 3740 (1902)]. For example, NdO_2 (or Nd_2O_4) is said to be formed by heating the oxalate in an atmosphere of oxygen. Other investigations have failed to find a higher oxide of neodymium, and some doubt remains as to its existence [Pangel and Brinton, *J. Am. Chem. Soc.*, **51**, 42 (1929)].

Tetrapositive cerium is well known. The dioxide is the common oxide, and numerous tetrapositive compounds will be encountered later. No higher valences for the rare earths other than those discussed here appear to have been found.

The situation as to the existence of the dipositive state is clear as respects europium, ytterbium, and samarium. These elements exhibit well-characterized dipositive states in both aqueous solution and the solid state. The stability decreases in the order of listing; dipositive samarium is extremely unstable in solution. The preparation and properties of these compounds will be discussed more fully in Chapter 6. It is certain that other dipositive states in the group are considerably less stable, but several pieces of evidence indicate their existence.

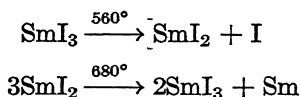
One of the standard methods for the preparation of the dipositive rare-earth compounds is reduction of an anhydrous halide at an elevated temperature by hydrogen. The approximate temperatures at which reduction begins are 400°C for SmCl_3 , 270° for EuCl_3 , and 560° for YbCl_3 . If anhydrous chlorides of the other metals are heated in hydrogen, some free metal is obtained rather than the dichloride. The percentage of free metal obtained on heating anhydrous chlorides in a hydrogen atmosphere at $880\text{--}920^\circ$ for ten hours was as follows [Jantsch, Skalla, and Grubitsch, *Z. anorg. allgem. Chem.*, **216**, 75 (1933)]:

COMPOUND	PER CENT FREE METAL
LaCl_3	1-2
NdCl_3 (840°)	1
GdCl_3	20
TmCl_3	24
LuCl_3	16

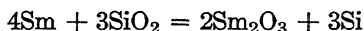
The metal was obtained as an alloy with the gold boat.

It will be noted that thulium trichloride gives the highest percentage of metal at 900° . It was also found that if thulium trichloride was heated at 650° some metal was obtained, and the compound became slightly colored and evolved some hydrogen from water. The other compounds did not behave in this way. The reactions are reductions

rather than thermal decomposition, since heating in argon under like conditions did not affect the compounds. The dipositive state is probably an intermediate state in the reduction, as under certain conditions samarium metal is found in addition to samarium dichloride during the reduction of samarium trichloride. It has also been shown [Jantsch and Skalla, *Z. anorg. allgem. Chem.*, **193**, 391 (1930)] that the thermal decomposition of samarium triiodide proceeds as follows:



The metal immediately either forms an alloy, or, if in a silica boat, the oxide:



Reduction by hydrogen thus does not seem to be a satisfactory method for preparation of the dipositive state for the rare-earth elements other than europium, ytterbium, and samarium. Many attempts at electrolytic reduction in solution have failed. Nevertheless, it has been reported that divalent compounds of La, Ce, Pr, Nd, Gd, and Tm can be prepared by the action of a strontium amalgam on a concentrated aqueous solution of the rare-earth sulfate, the divalent sulfate formed being stabilized by occlusion in the strontium sulfate [Holleck and Noddack, *Angew. Chem.*, **50**, 819 (1937); Holleck, *Atti X° Congr. intern. chim.*, **2**, 671 (1938), through *Chem. Abst.*, **33**, 8064 (1939)]. These experiments have not yet been confirmed, and full details are not available.

This brief survey of the available evidence shows that in general the oxidation states given in Table 2 are well supported. Many particular points require further investigation, but it seems clear that the predicted electronic structures are in satisfactory accord with the observed chemical facts. It must now be seen whether the postulated structures also explain the physical facts.

Chapter 2

PARAMAGNETIC PROPERTIES OF RARE-EARTH COMPOUNDS

One of the outstanding properties of the rare earths is the strong paramagnetism displayed by the metals and their compounds. Not only have magnetic methods been valuable for identification and the determination of purity, but also they have cast considerable light on the configurations of the ions in various states of oxidation and reduction.

The calculation of susceptibilities for magnetically dilute substances has been discussed in the notable book by Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford, Oxford University Press, 1932. The formulas given there are found to apply well to many rare-earth compounds, especially the highly hydrated salts. The reason is chiefly that the paramagnetism arises from the 4f electrons which are shielded to a considerable extent from the fields produced by the adjacent chemically bonded groups. To apply the formulas given, however, the proper quantum numbers L , S , and J must be known. For the rare earths there is a paucity of the direct spectroscopic evidence necessary to establish the "lowest lying" spectral terms; this information can be obtained, however, by means of Hund's rule (see Chapter 1). In addition to this rule, something must be known about the dependence of the energy on the inner quantum number J in order that the proper expression for μ and α may be selected; that is, it must be known whether the separation of the multiplet components is small, of the same order of magnitude, or large, compared to kT .

The fact that the paramagnetism of rare-earth ions arises from the 4f electrons is apparent when the experimental susceptibilities are compared with those theoretically calculated on the assumption that the number of electrons in the 4f states increases from zero for lanthanum to fourteen for lutecium. Table 4 gives the theoretical values calculated by Hund [*Z. Physik*, **33**, 855 (1925)], and by Van Vleck and Frank [*Phys. Rev.*, **34**, 1494, 1625 (1929)], together with the experimental values of certain investigators. These experimental values of μ_{eff} are derived from the measured susceptibility by the following formula:

$$\chi_m = N_0\alpha + \frac{N_0\mu_{\text{eff}}^2}{3kT}$$

where χ_m is the molal susceptibility, N_0 is Avogadro's number, T is the absolute temperature, and k is the gas constant per molecule. The $N_0\alpha$ term is a small, negative, diamagnetic contribution for which a correction is usually applied. The paramagnetic term is in the form of Curie's law, $\chi_m = C/T$, with $C = \frac{N_0\mu_{\text{eff.}}}{3k}$, the Curie constant. The

effective moment, $\mu_{\text{eff.}}$, in Bohr magnetons, $\mu_0 = \frac{eh}{4\pi mc}$, is given by

$$\mu_{\text{eff.}} = \sqrt{\frac{3k\chi_m T}{N_0}} = 2.84\sqrt{C}$$

If Weiss's law holds, $\chi_m = C/(T + \Delta)$, the effective moment is calculated from a similar expression,

$$\mu_{\text{eff.}} = \sqrt{\frac{3k\chi_m(T + \Delta)}{N_0}} = 2.84\sqrt{C}$$

The Δ in Weiss's law arises through interactions between the paramagnetic atoms. It is greater for the more highly condensed systems such as the metals themselves or their oxides and is generally small in the hydrated salts where the paramagnetic atoms are far apart. The Δ correction is frequently neglected as its evaluation requires the measurement of susceptibility over a considerable range of temperatures—a more difficult experimental problem than its measurement at room temperature. Unless the atom is in an S state, neglect of Δ may result in appreciable error in the calculated effective moment; thus, Δ for neodymium compounds is not less than about 45° , even at high magnetic dilution.*

The smaller and larger values given in Table 4 for samarium and europium in the column headed "V. V. and F." were obtained by taking 33 and 34 respectively for the screening number, an assumption that will be discussed presently. The experimental results differ from one another not only because different investigators used different estimates of the diamagnetic corrections and slightly different values of the physical constants but also because the sources of the compounds were different, and purification is difficult.

* Professor P. Selwood has pointed out a good example of the effect of neglecting the Δ term in manganic phosphate. The theoretical $\mu_{\text{eff.}}$ for the Mn^{+++} ion is 4.90 Bohr magnetons. When the simple Curie law is assumed the much lower value 4.49 is obtained for the moment. However, manganic phosphate follows the Weiss law with $\Delta = 53^\circ$, and recalculation of $\mu_{\text{eff.}}$ on this basis gives a value 4.89 in excellent agreement with the theoretical value for four unpaired electrons.

TABLE 4
EFFECTIVE BOHR MAGNETON NUMBERS OF RARE-EARTH TRIPOSITIVE IONS

Tripositive Ion	Theoretical μ_{eff} .			Experimental μ_{eff} .						
	Term	Hund	V. V. and F.	Meyer	Cabrera	Zernicke and James	Decker	Williams	Cabrera and Duperier	Leiden
La	$1S$	0.00	0.00					diam.		2.51
Ce	$4f^2 \text{}^3F_{7/2}$	2.54	2.56	2.77	2.39	2.37	2.10	0.23?		
Pr	$4f^3 \text{}^3H_4$	3.58	3.62	3.47	3.62	3.47	3.41	2.29?	3.47	
Nd	$4f^3 \text{}^4I_{9/2}$	3.62	3.68	3.51	3.62	3.52	3.45	3.43	3.52	
61	$4f^4 \text{}^5I_4$	2.68	2.83							
Sm	$4f^5 \text{}^6H_{5/2}$	0.84	1.55-1.65	1.32	1.54	1.53	1.63	1.57	1.58	
Eu	$4f^6 \text{}^7F_0$	0.00	3.40-3.51	3.12	3.61	7.81	7.86	7.46	3.54	7.8
Gd	$4f^7 \text{}^8S_{7/2}$	7.94	7.94	8.1	7.95	9.4	9.8		9.6	
Tb	$4f^8 \text{}^7F_6$	9.7	9.7	9.0	9.6	9.4	10.9	10.0	10.3	
Dy	$4f^9 \text{}^6H_{15/2}$	10.6	10.6	10.6	10.5		10.4	10.1	10.4	10.6
Ho	$4f^{10} \text{}^5I_8$	10.6	10.6	10.4	10.5	10.3	10.4	9.2	9.4	9.0
Er	$4f^{11} \text{}^4I_{15/2}$	9.6	9.6	9.4	9.55	9.0	9.5		7.0	
Tm	$4f^{12} \text{}^3H_6$	7.6	7.6	7.5	7.2	4.4	4.5		4.3	
Yb	$4f^{13} \text{}^2F_{7/2}$	4.5	4.5	4.6	4.4	diam.	4.5	0.49?		
Lu	$4f^{14} \text{}^1S$	0.00	0.00	diam.		diam.	1.2?			

St. Meyer, *Physik. Z.*, **26**, 51, 478 (1925); Cabrera, *Compt. rend.*, **180**, 668 (1925); *J. chim. phys.*, **36**, 237 (1939); Zernicke and James, *J. Am. Chem. Soc.*, **48**, 2827 (1926); Decker, *Ann. Physik*, **79**, 324 (1926); Williams, *Phys. Rev.*, **12**, 158 (1918), **14**, 348 (1919), **27**, 484 (1926); Cabrera and Duperier, *Compt. rend.*, **186**, 1640 (1928); Leiden investigators, *Leiden Communications*, 122a, 128b, 132e, 140d, 167b, 167c, 168a, 201b, 210c. The older measurements of Du Bois, Urban, and Wedekind are omitted; a summary of all work up to 1926 is given in the paper by Zernicke and James. The results of Freed, *J. Am. Chem. Soc.*, **52**, 2702 (1930), give $\mu_{\text{eff}} = 1.57$ for Sm at room temperature. Sucksmith, *Phil. Mag.*, (VII) **14**, 1115 (1932), has also made measurements which agree well with the Van Vleck calculations.

St. Meyer, Cabrera, and Zernicke and James made their measurements on hydrated sulfates of the type $R_2(SO_4)_3 \cdot 8H_2O$; Decker employed solutions of sulfates and nitrates; Williams used oxides; and Cabrera and Duperier measured oxides and anhydrous sulfates. The Δ correction was usually neglected; the generally fair agreement indicates that the molecular field forces on the $4f$ electrons are not of great significance. The data of Table 4 have been plotted in Fig. 2. The agreement between experiment and theory is remarkably good; Hund's

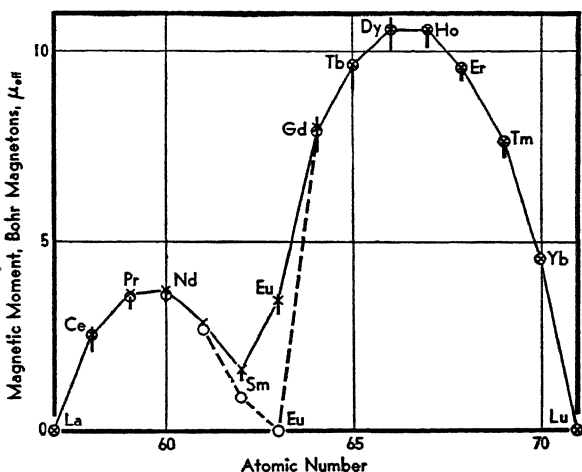


FIG. 2. Magnetic moments of the tripositive rare-earth ions. The dotted lines show Hund's earlier predicted values for 61, samarium, and europium.

values for samarium and europium are too small. Hund and also Laporte [*Z. Physik*, **47**, 761 (1928)] felt that these two discrepancies might be due to the multiplet intervals of samarium and europium not being really very large compared to kT , as had been assumed, but it remained for Van Vleck and Frank [*loc. cit.*] to investigate the multiplet structures and recalculate the susceptibilities of these two elements.

These authors pointed out that the various multiplet components are not evenly spaced, but rather crowd together for small values of J , and, indeed, that the separation between components with the two lowest values of J may be of the same order of magnitude as kT . Figure 3 presents the Grottrian energy-level diagrams for samarium and europium, showing the small separations, together with diagrams for praseodymium and terbium for which the assumptions of Hund are valid.

For samarium and europium (and also element 61) the contribution to the magnetic susceptibility from J states other than the lowest is

therefore considerable, and the accurate "intermediate" Van Vleck formula, including the second-order Zeeman terms, must be used for

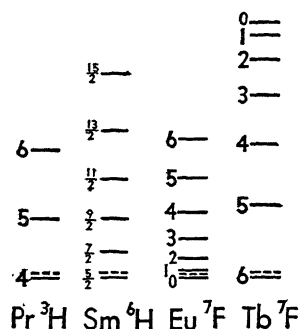


FIG. 3. Grottrian energy levels for praseodymium, samarium, europium, and terbium. The value of J is shown for each level.

the calculation of the susceptibility. To use this formula the multiplet intervals must be quantitatively evaluated from the screening constant. The screening constant is usually obtained from X-ray data, but X-ray emission lines arising from transitions from the $4f$ level are found only after this level is complete; hence the screening constant must be indirectly determined from atoms heavier than the rare earths. The resulting uncertainty of this method is that the screening constant may be either 33 or 34, numbers in the ranges 30–32 and 35–38 being incompatible with experimental measurements on samarium. Either value for the screening constant results, how-

ever, in a calculated susceptibility for both samarium and europium which agrees well with the experiments.

Although the tripositive lanthanum ion should be diamagnetic with no temperature coefficient of susceptibility, recent magnetic measurements on the sulfate, oxalate, and oxide indicate that there is a small temperature-dependent paramagnetic residue which cannot be accounted for on the basis of paramagnetic impurities or nuclear spin contribution [Haller and Selwood, *J. Am. Chem. Soc.*, **61**, 85 (1939)]. The explanation which has been advanced is that there is a "surface" paramagnetism, due perhaps to the high electric dissymmetry of the surface, since it has been observed that the surface affects the susceptibility somewhat. A similar effect in zinc oxide disappears upon sintering the material, that is, upon diminishing the surface. The matter is not entirely clear, however. The fact that there is a small measurable orthopara hydrogen conversion on pure lanthanum oxide surfaces [Taylor and Diamond, *J. Am. Chem. Soc.*, **57**, 1251 (1935)] seems difficult to explain unless some paramagnetism arises from the molecules themselves.

Except for samarium, europium, and element 61, the rare earths should obey Curie's law at least roughly and should have a temperature coefficient, $-\frac{1}{\chi} \frac{d\chi}{dT} \approx \frac{1}{T}$, of about $1/293$ at room temperature. In Table 5 are given the reciprocals of some experimentally determined

temperature coefficients at or near room temperature. In most of them the deviation from 293 is not large and may be attributed to the presence of small interatomic forces in the solid. Curie's law is thus

TABLE 5
RECIPROCAL OF SUSCEPTIBILITY TEMPERATURE COEFFICIENTS
(ROOM TEMPERATURE)

	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Anhydrous sulfates												
Cabrera	...	344	341	500	292	296	304	301	304	322	369
Hydrated sulfates												
Z. and J.	290	358	348	1700	...	305	327	...	320	252	...	292
Oxides												
Cabrera	...	366	344	522	306	316	312	307	308	330	390
Williams	337	1600	...	305	...	308	...	306

roughly obeyed at room temperature and often over a considerable range. Except for possible anomalies at very low temperatures, the Weiss modification, $\chi = C/(T + \Delta)$, of the Curie law holds well over a range of a few hundred degrees. For example, Dy_2O_3 , CeF_3 , and $\text{Er}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ have been measured down to 14°K and $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ down to 1.3°K at Leiden, and all obey the Curie-Weiss law very well with the exception of CeF_3 , for which there are deviations below 65°K ; the values of Δ are 16, 62, 1.9, and 0.0 (or possibly 0.26), respectively. It has been shown that deviations from the Curie-Weiss law should become apparent when the temperature becomes so low that the energy required to turn over an atom against the molecular field becomes comparable with kT .

Dipositive europium is isoelectronic with tripositive gadolinium. The Curie-Weiss constants of these two ions [Selwood, *J. Am. Chem.*

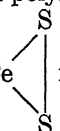
TABLE 6
CURIE-WEISS CONSTANTS OF DIPOSITIVE EUROPIUM AND TRIPROPOSITIVE GADOLINIUM

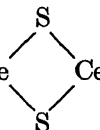
$T^\circ \text{K}$	$\chi_{\text{Eu}}(T + 4)$ in EuSO_4	$\chi_{\text{Gd}}(T + 2)$ in $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	$\chi_{\text{Gd}}(T + 18)$ in Gd_2O_3
343	7.64	8.11	7.63
293	7.66	8.11	7.62
223	7.64	8.09	7.62
153	7.62	8.08	7.63
83	7.63	8.10	7.60

Soc., **55**, 4869 (1933)] are compared in Table 6. A diamagnetic correction has been applied to the results. The values for the sulfate and oxide show the effect of varying the type crystal. Not only are the susceptibilities nearly the same for the two ions, but the molecular

field interaction constants Δ are also approximately equal. The conclusion is that dipositive europium has the same electronic configuration as tripositive gadolinium.

Some mention has already been made of the usefulness of the rare-earth magnetic properties. Klemm, Meisel, and von Vogel [*Z. anorg. allgem. Chem.*, **190**, 133 (1930)] measured the susceptibility of the compound Ce_2S_4 , and showed that it was a polysulfide of tripositive cerium

with the likely structure $\text{S}=\text{Ce}-\text{S}-\text{Ce}$  rather than a simple sulfide

of tetrapositive cerium with a possible structure $\text{S}=\text{Ce}$  $\text{Ce}=\text{S}$.

The susceptibility is the same as that of Ce_2S_3 , whereas if the cerium were tetrapositive the susceptibility would differ appreciably from that of cerium sesquisulfide, being then about the same as that of lanthanum sesquisulfide. This is an example of one kind of rare-earth chemical problem which can be successfully treated by a magnetic method.

An important use which has been made of the magnetic properties of rare earths is the attainment and measurement of extremely low temperatures.* For example, if gadolinium sulfate octahydrate is placed in a magnetic field it becomes warm. At room temperature the increase in temperature is very small, but, if the octahydrate is cooled to the temperature of boiling helium and a magnetic field of 20,000

*Since the magnetization M of a substance is a function of the temperature T and other thermodynamic variables, the two principal laws of thermodynamics may be invoked to obtain relations among the variables. If P , V , E , H , and S are the pressure, volume, energy, magnetic field strength, and entropy of the system under consideration, then the first and second laws require that

$$dS = \frac{dE + PdV - HdM}{T}$$

But $S = S(P, T, H)$ and, therefore,

$$dS = \left(\frac{\partial S}{\partial T}\right)_{P, H} dT + \left(\frac{\partial S}{\partial P}\right)_{T, H} dP + \left(\frac{\partial S}{\partial H}\right)_{P, T} dH$$

Consequently, at constant pressure and entropy

$$\left(\frac{\partial S}{\partial T}\right)_{P, H} \left(\frac{\partial T}{\partial H}\right)_{S, P} = -T \left(\frac{\partial S}{\partial H}\right)_{P, T}$$

or

$$C_{P, H} \left(\frac{\partial T}{\partial H}\right)_{S, P} = -T \left(\frac{\partial S}{\partial H}\right)_{P, T}$$

gauss employed, the increase in temperature is comparatively large. Hence, if the octahydrate is allowed to impart this energy to the surroundings, for example, by evaporating the liquid helium, and is then isolated thermally from the liquid helium bath and the magnetic field removed, the adiabatic demagnetization must result in a lowering of the temperature of the octahydrate and the vessel in contact with it. This method of attaining temperatures lower than those obtainable with liquid helium was independently proposed by Giauque and by Debye [Giauque, *J. Am. Chem. Soc.*, **49**, 1864 (1927); Debye, *Ann. Physik*, **81**, 1154 (1926)]. A temperature of 0.29°K was reached by Giauque and McDougall in the Berkeley laboratory, using $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. Other compounds, such as cerium sulfate, dysprosium ethyl sulfate, and cerium fluoride, have been used to attain temperatures close to 0.09°K . However, the lowest temperature yet attained by the magnetocaloric method, 0.004°K , was reached at the Leiden laboratory with the aid of a mixture of potassium alum and chrome alum.*

where $C_{P, H}$ is the heat capacity at constant P and H . Because $\left(\frac{\partial S}{\partial H}\right)_{P, T} = \left(\frac{\partial M}{\partial T}\right)_{P, H}$,

$$C_{P, H} \left(\frac{\partial T}{\partial H}\right)_{S, P} = -T \left(\frac{\partial M}{\partial T}\right)_{P, H}$$

Now $M = \chi H$, and if Curie's law is obeyed $\chi = C/T$. Accordingly

$$C_{P, H} \left(\frac{\partial T}{\partial H}\right)_{S, P} = \frac{CH}{T}$$

where $\left(\frac{\partial T}{\partial H}\right)_{S, P}$ is the temperature change attending a reversible, adiabatic change in the field H in which the substance is immersed. When H is large and T low so that $\frac{\mu H}{kT}$ is large (μ = magnetic moment of the ion or molecule of interest) then a more exact expression for χ is

$$\chi = \frac{N_0 \mu}{H} \left\{ \coth \frac{\mu H}{kT} - \frac{kT}{\mu H} \right\}$$

(See Bates, *Modern Magnetism*, Cambridge University Press, 1939, for references to the work of Weiss and Forrer, Giauque, and Debye.)

* This temperature value depends on an extrapolation of Curie's law and may, therefore, be in error.

Chapter 3

ABSORPTION SPECTRA OF RARE-EARTH COMPOUNDS

Solutions of many rare-earth compounds have sharply defined absorption bands in the infrared, visible, and ultraviolet portions of the spectrum and consequently show a variety of colors. The relative intensities of the bands in the commonly observed portion of the spectrum are seen in Fig. 4, which shows the spectra of the rare-earth chlorides in slightly acid solution [Prandtl and Scheiner, *Z. anorg. allgem. Chem.*, **220**, 107 (1934)]; the chlorides were chosen because the chloride ion shows no absorption in this region. Since the visible portion of the spectrum is from about 3900 to 7700 Å, tripositive cerium and gadolinium are completely colorless, as are lanthanum, ytterbium, and lutetium, which are not shown.

The marked periodicity in the colors of the ions has led many people to suggest correlations between color and electronic structure. Main Smith in 1927 (*Nature*, **120**, 583) pointed out that the colors of the solutions of the first seven tripositive ions are similar to those of the last seven in reverse order, and that this fact is related to the electronic configurations of the ions, an ion having n electrons more than lanthanum being the same color as the one having $14 - n$ electrons more. This is equivalent to saying in spectroscopic language that ions having electronic ground states different only in the inversion of the J value have similar colors; this relationship is shown in Table 7.

TABLE 7

COLORS AND GROUND STATES OF THE TRIPROPOSITIVE RARE-EARTH IONS

Ion	Atomic		Color	Color	Ground		Ion
	No.	State			State	No.	
La ⁺⁺⁺	57	¹ S ₀	Colorless	Colorless	¹ S ₀	71	Lu ⁺⁺⁺
Ce ⁺⁺⁺	58	² F _{5/2}	Colorless	Colorless	² F _{7/2}	70	Yb ⁺⁺⁺
Pr ⁺⁺⁺	59	³ H ₄	Yellow-green	Pale green	³ H ₆	69	Tm ⁺⁺⁺
Nd ⁺⁺⁺	60	⁴ I _{9/2}	Red-violet	Rose	⁴ I _{15/2}	68	Er ⁺⁺⁺
61 ⁺⁺⁺	61	(⁵ I ₇)	Brownish yellow	⁵ I ₈	67	Ho ⁺⁺⁺
Sm ⁺⁺⁺	62	⁶ H _{5/2}	Pale yellow	Pale yellow-green	⁶ H _{15/2}	66	Dy ⁺⁺⁺
Eu ⁺⁺⁺	63	⁷ F ₀	Pale pink	Very pale pink	⁷ F ₆	65	Tb ⁺⁺⁺
Gd ⁺⁺⁺	64	⁸ S _{7/2}	Colorless]				

It is clear, however, that the consideration of the ground states alone can provide only a very qualitative explanation of the observed spectra.

The non-tripositive ions, for instance, have the same configurations and, therefore, the same ground states as the isoelectronic tripositive ions, but the colors are quite different, as may be seen from Table 8.

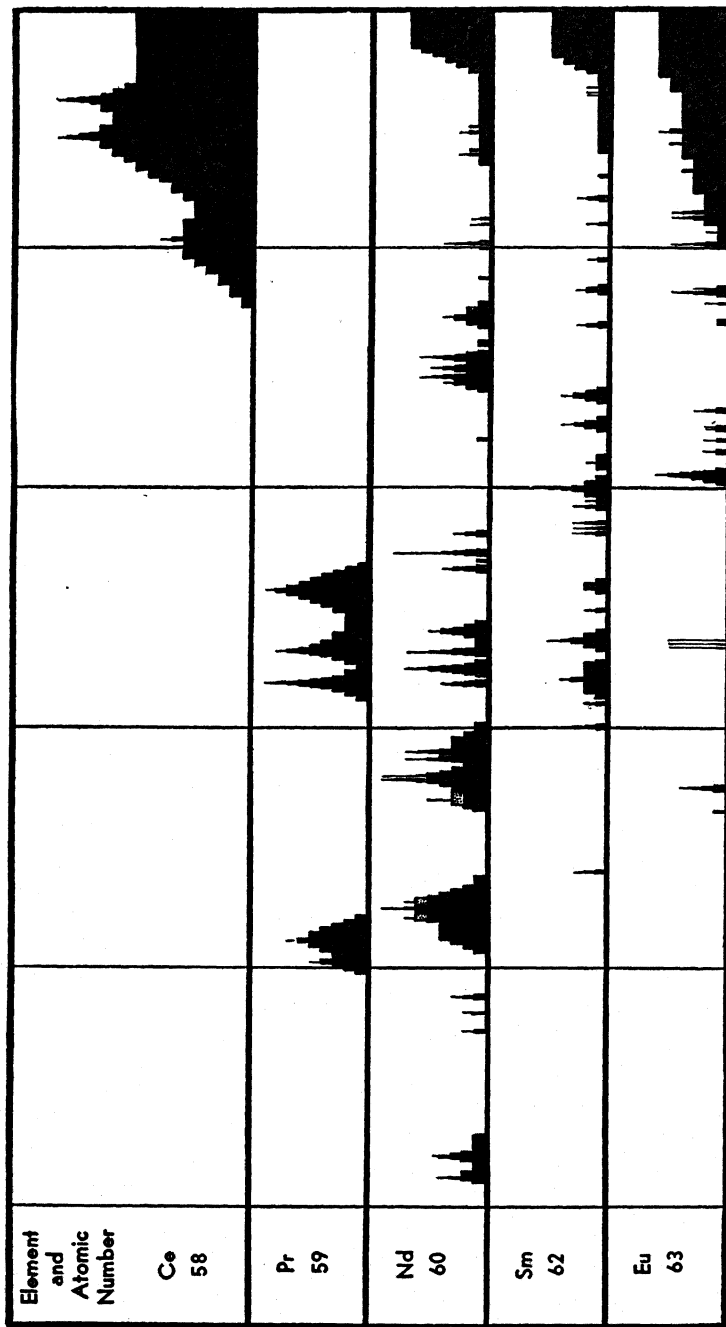
TABLE 8
COLORS OF NON-TRIPOSITIVE RARE-EARTH IONS

Ion	Color	Isoelectronic Ion	Color
Ce ⁺⁺⁺⁺	Orange-red	Lu ⁺⁺⁺	Colorless
Pr ⁺⁺⁺⁺	Black in the solid oxide	Ce ⁺⁺⁺	Colorless
Sm ⁺⁺	Deep red-brown	Eu ⁺⁺⁺	Pale pink
Eu ⁺⁺	Pale straw color	Gd ⁺⁺⁺	Colorless
Tb ⁺⁺⁺⁺	Brown in the solid oxide	Gd ⁺⁺⁺	Colorless
Yb ⁺⁺	Green	Lu ⁺⁺⁺	Colorless

Only a detailed analysis of the energy levels of the ions and of the nature of the radiation based on extensive experimental data can lead to a true understanding of these spectra. The bands of the non-tripositive ions of the rare-earth group have not been extensively studied, and the few investigations that have been made [McCoy, *J. Am. Chem. Soc.*, **58**, 1577 (1936), Eu⁺⁺] reveal only broad diffuse bands without the resolvable structure found to be characteristic of the bands of most of the tripositive ions. Therefore the remainder of this chapter will be devoted to a discussion of the observation and interpretation of the spectra of the tripositive rare-earth ions in crystals and in solution.

The precise knowledge of the energy levels and other properties of a great many molecules and atoms in the gaseous state is derived largely from the observation and detailed interpretation of their line spectra. In general, however, this source of information is not available for material in solution or in the solid state. Absorption bands, if they exist at all, are usually broad and diffuse with no resolvable structure. Therefore the rare-earth compounds (and a few compounds of the transition elements) are especially distinctive in that their absorption bands have been found to consist of a considerable number of fairly sharp lines. Indeed, at low temperature (liquid-air temperature or lower) the line widths compare favorably with those in the absorption spectra of gases. The possibility thus presented for quantitative measurements of energy levels provides not only the data for calculating such quantities as the magnetic susceptibilities and the electronic specific heats for the rare-earth compounds themselves but also a most valuable testing ground for theories of the solid state.

The spectra of the rare-earth ions, observed either in absorption or fluorescence, contain lines that may be separated roughly into four



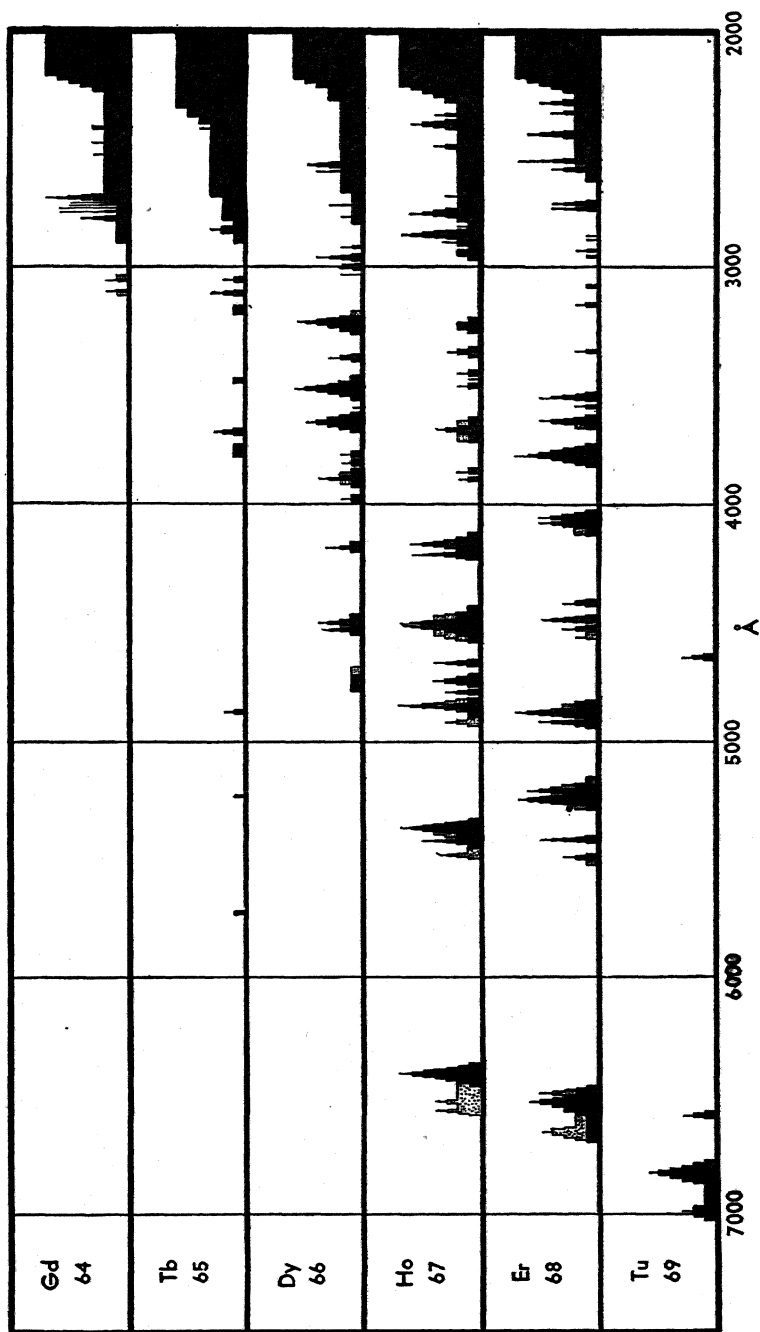


Fig. 4. Absorption spectra of rare-earth trichlorides.

main classes: (1) strong, sharp lines occurring in widely separated groups; (2) weak, sharp lines, frequently occurring as satellites on the violet side of the strong, sharp lines; (3) weak, diffuse lines usually lying on the violet side of the strong, sharp lines also; and (4) strong, diffuse bands in the ultraviolet showing no structure. From the energy of the radiation it is evident that electronic transitions are involved. It would be expected that the strong, sharp lines would correspond to pure electronic transitions, and that the weaker lines would arise from the superposition of other energy levels upon the electronic levels. Consequently the lines of the first class are considered now, the weaker lines being ignored for the moment.

The general method of treatment is to consider the rare-earth ion as though it were a free ion situated in an electric field provided by the neighboring atoms and ions. The assumption is made that the interactions of the electrons of the ion with one another are much stronger than their interaction with the external field. If this is so, the system may legitimately be treated by the well-developed methods for the Stark and Zeeman effects of atomic spectra, the expected energy levels of the free ion being used as a basis. The unperturbed energy-level diagram should then explain the groups of sharp, strong lines.

However, even the fundamental question of the origin of the lines is a difficult one. The magnetic measurements and other evidence already discussed show the ground configuration of the trivalent ions to be $4f^n$. A term belonging to this configuration must therefore be the lower level in absorption. For the upper term two possibilities arise. The first is that it is a term belonging to another configuration, e.g., $4f^{n-1}5d$ or $4f^{n-1}5g$. The second possibility is that the upper state belongs to the same configuration, $4f^n$, and differs from the lower level only in having a different quantum number L or S while the values of the l 's for the individual electrons are unchanged. With the first possibility the radiation would be produced as usual in atomic spectra by a change in the electric dipole of the atom (electric dipole radiation). If the second possibility is correct, the transition would be, in free atoms, a "forbidden" transition for electric dipole radiation by the Laporte selection rule which states that the algebraic sum of individual l 's must change by an odd integer. The evidence strongly indicates that the second possibility is correct in respect to the sharp lines and that the transitions are forbidden transitions. Most workers in the field now accept this viewpoint. The transitions would be allowed, however, with faint intensity by considering quadrupole or magnetic dipole radiation or distortion of the symmetry of the atom by the crystal field. The chief evidence in support of the forbidden transition

hypothesis may be briefly summarized [Freed, *Phys. Rev.*, **38**, 2122 (1931); Van Vleck, *J. Phys. Chem.*, **41**, 67 (1937)]:

1. If the sharp lines do correspond to transitions between various terms of the $4f^n$ configuration, no sharp lines are to be expected from cerium and ytterbium with the configurations $4f$ and $4f^{13}$ respectively. For these configurations only one L value is possible, and two would be needed to provide both an upper and lower state. Any lines occurring in these elements would then necessarily correspond to the first possibility—a change of configuration. This involves an outer state used for chemical bonds, and the resulting large perturbations would be expected to cause a marked broadening of the lines. It is observed [Freed and Mesirov, *J. Chem. Phys.*, **5**, 22 (1937)] that cerium and ytterbium show only diffuse bands in the ultraviolet.

2. Although at first sight the sharp-line absorption seems relatively strong, actual measurements of intensity support the view that forbidden transitions are involved. It is found that the intensity of the lines is only about a millionth that expected for electric dipole radiation. Most of the lines would be undetected in a low-pressure gas, but the high density of the solid increases the intensity factor a millionfold or so. The high intensity of lines due to dipole radiation relative to that of lines from forbidden transitions provides a qualitative explanation of the great persistence of the ultraviolet bands of cerium compared to the bands of the other rare earths shown in Fig. 4. By the first argument the cerium bands are dipole radiation.

3. It should be possible to make quantum-mechanical calculations of the expected positions of the unperturbed levels of the ions. Good agreement would be powerful support for the forbidden-transition hypothesis. Although it has not yet been possible to do this for many elements, a promising beginning has been made with thulium and praseodymium [Bethe and Spedding, *Phys. Rev.*, **52**, 454 (1937); Spedding, *Phys. Rev.*, **58**, 255 (1940)]. The authors note the important point that it is not satisfactory to assume Russell-Saunders coupling for the ions, but that spin-orbit interactions including perturbations must be taken into account. For the upper levels it was found that Russell-Saunders coupling is far from being obeyed, as the perturbations amounted to as much as $10,000\text{ cm}^{-1}$. Fairly satisfactory agreement was found with the levels experimentally observed as shown in Table 9. It should be cautioned that a limited numerical agreement is not necessarily conclusive as the spectra are very complex. Calculations made assuming Russell-Saunders coupling give somewhat different results, which may also be fit by the available data [Lange, *Ann. Physik*, **31**, 609 (1938)].

TABLE 9

COMPARISON OF CALCULATED AND OBSERVED TERMS FOR Pr^{+++} AND Tm^{+++}

Term (Pr^{+++})	Calculated cm^{-1}	Observed cm^{-1}	Term (Tm^{+++})	Calculated cm^{-1}	Observed cm^{-1}
3H_4	0	0	3H_6	0	0
3H_5	2,239		3H_4	5,565	
3F_2	4,496	4,750	3H_5	8,490	8,248 ¹
3H_6	4,562	5,650	3F_2	10,740	12,750 ¹
3F_3	6,359	5,950	3F_4	13,372	14,600
3F_4	7,030	7,250	3F_3	14,560	15,150
1G_4	10,406	9,469	1G_4	22,580	21,500
1D_4	10,878	10,200	1D_2	23,730	21,100
1I_6	17,046	16,630	1I_6	27,680	28,000
		17,480			
3P_0	20,560	20,660	3P_0	32,155	35,000 ¹
		20,910			
3P_1	21,469	21,150	3P_2	35,020	36,300 ¹
		22,305			
3P_2	22,512	22,810	3P_1	35,290	38,000 ¹
		24,050			
1S_0	36,144		1S_0	57,425	

¹ These bands were observed subsequent to the calculation of the expected positions.

It is a characteristic of the rare-earth spectra that considerably more lines are found than can be accounted for by the unperturbed electronic energy levels. At least a partial explanation is that the crystal field produced by neighboring atoms gives rise to a Stark effect which partially or wholly removes the degeneracy of the levels, thus giving rise to more lines. This effect has been investigated theoretically by Bethe [*Ann. Physik*, (5) 3, 133 (1929)], using the methods of group theory. The number of component levels induced from the terms of the unperturbed ion by electric fields of various symmetries is given in Table 10.

TABLE 10

TERM SPLITTING BY CRYSTAL FIELDS

Symmetry of Field	J	Number of Component Levels												
		0	1	2	3	4	5	6	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$
Cubic or higher symmetry	1	1	2	3	4	4	6	1	1	2	2	3	4	
Hexagonal	1	2	3	5	6	7	9	1	2	3	4	5	6	
Tetrahedral, rhombic, or lower symmetry	1	3	5	7	9	11	13	1	2	3	4	5	6	

The $(2J + 1)$ degeneracy is removed entirely by rhombic fields for atoms with an even number of electrons; for all atoms with an odd

number there remains a twofold degeneracy [the Kramers degeneracy, Kramers, *Proc. Amster. Acad. Sci.*, **33**, 959 (1930)] which may not be removed by an electric field of any symmetry whatever.

An excellent test of the applicability of Bethe's theory to the rare-earth ions has been made by Freed and Weissman [*J. Chem. Phys.* **8**, 878 (1940)], who examined three groups of lines in the absorption spectra of europium trifluoride crystals, in which there is known to be a symmetry of C_{2v} about the europic ions, and of europium trifluoride in a cubic mixed crystal with bismuth trifluoride, in which the symmetry about the metal ion is cubic holohedral, O_h . The three groups of lines had been assigned by Gobrecht [*Ann. Physik*, **28**, 673 (1937)] to transitions between a higher state with $J = 0$ and lower states with $J = 0, 2$, and 3 . The number of lines in each group was found to correspond exactly to the crystallographic symmetry and the theoretically derived number of levels. For example, the $J = 0$ to $J = 2$ transition shows five lines in europium trifluoride but only two in an $\text{EuF}_3\text{-BiF}_3$ cubic mixed crystal. [See the review by Freed, *Rev. Modern Phys.*, **14**, 105 (1942).]

Bethe's theory should also be directly applicable to the derivation of the number of low-lying levels (levels less than about 600 cm^{-1} above the ground level) in the ion. These low-lying levels come from the splitting of the ground term or, in europium and samarium, of the next higher term, and are particularly important in determining heat capacities and magnetic susceptibilities at low temperatures. The number and positions of these levels may be spectroscopically determined. The experimental procedure is to photograph the spectrum over a range of temperatures, e.g., $14\text{--}300^\circ\text{ K}$. In the spectrum at 14° K practically all the lines originate in the lowest electronic level since there is no appreciable population in any level unless it is very close to the lowest one. In comparing the 14° K spectrum with that at 78° K one may find some lines enhanced in intensity. Such lines must originate in levels whose population has been increased by the rise in temperature. A correlation of an intensity versus temperature plot with the population of an assumed level as given by the Boltzmann distribution law gives the approximate positions of the levels. The lines originating in the basic and low-lying levels and terminating in a common upper level are separated from one another by the intervals between the low-lying states; these constant-frequency intervals give quantitatively the positions of the levels.

The method is usually limited to levels situated within $300\text{--}400\text{ cm}^{-1}$ of the lowest, since exorbitant thicknesses and exposure times are required to bring out the thinly populated higher levels. In general the

positions of the observed lines are shifted about 10 cm^{-1} to longer wavelengths in going from 300° K to 78° K , although the positions of the levels are not much affected. In many hydrated compounds the levels found are essentially independent of the compound investigated. In $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{EuBr}_3 \cdot 6\text{H}_2\text{O}$, and $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ at room temperature, the levels found are (I) 305, 304, 306; (II) 394, 384, 383; (III) 422, 440, 435; and (IV) 970, 971 and 983 cm^{-1} respectively. In $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ they are (I) 62, 72; and (II) 250, 260 cm^{-1} respectively [Spedding, Hamlin, and Nutting, *J. Chem. Phys.*, **5**, 191 (1937)]; however, in $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Zn}_3\text{Nd}_2(\text{NO}_3)_{12}$, and

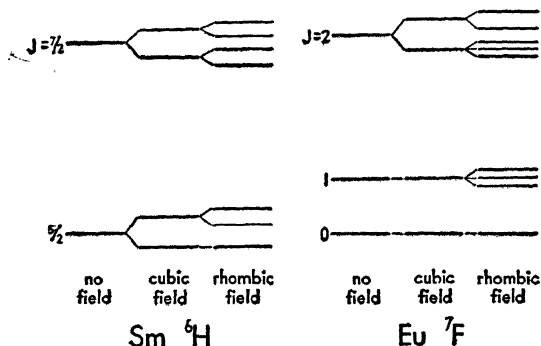


FIG. 5. Theoretical splitting of energy levels of samarium and europium by electrostatic crystal fields having cubic and rhombic symmetry.

$\text{Mg}_3\text{Nd}_2(\text{NO}_3)_{12}$ the lower level is found at 36.6, 33.6, and 30.2 cm^{-1} respectively [Ewald, *Ann. Physik*, **34**, 209 (1939)], showing that the nature of the compound may have a pronounced effect on the splitting, as indeed would be expected. The constancy of the levels in the hydrated salts is probably due to an essentially similar configuration of an octahedron of oxygen atoms about the metal ion in each compound.

The results of the spectroscopic investigations do not agree with the predictions of Bethe's theory in some instances. In samarium, levels are found at 0, 160, 188, 225, and perhaps 245 cm^{-1} [Spedding and Bear, *Phys. Rev.*, **46**, 975 (1934)], although an electric field cannot possibly split the $^5H_{7/2}$ ground state into more than three levels (Fig. 5 and Table 10). Supporting evidence for the presence of four levels is given by heat-capacity measurements on $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ [Ahlberg and Freed, *J. Am. Chem. Soc.*, **57**, 431 (1935)]. The heat capacity of the gadolinium compound comes entirely from lattice vibrations above 15° K . (Below 15° K there are deviations due to a slight splitting of the ground term [Kurti, *Z.*

Physik. Chem., B20, 305 (1933)]. If it is assumed that the lattice vibrations of the samarium compound are the same as those of the gadolinium one, any difference in heat capacity can be assigned to the activation of electronic levels in samarium. The observed difference is fit well by levels with equal statistical weights at 0, 160, 188, and 225 cm^{-1} (Fig. 6); three levels do not give a satisfactory fit. The discrepancy above 150° K is due to the presence of higher levels from the $^5H_{7/2}$ term in samarium.

Whether the presence of more levels than can be predicted implies a fundamental disagreement with the existing theory of these systems is

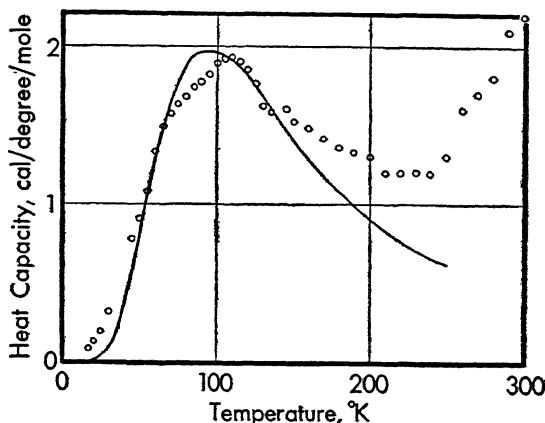


FIG. 6. The difference between the molal heat capacities of $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. Experimental values are represented by small circles; the full curve shows predictions of the theory.

not known. It is most probable, however, that the basic theory is correct and that the extra levels found are to be explained in some other way. They may be unusually strong vibrational lines due to some resonance phenomena or they may arise from the ions occupying two different crystallographic positions in the solid. More detailed determinations of crystal structure would aid considerably in interpreting the energy-level pattern.

An investigation of several hydrated europium salts has shown levels at 0, 300, 390, 938, 970, and perhaps 430 cm^{-1} [Spedding, Moss, and Waller, *J. Chem. Phys.*, 8, 908 (1940)]. The ground term of europium, 7F_0 , cannot be split. However, in europium as in samarium the next term lies relatively low as shown by the magnetic susceptibilities at room temperature (see p. 16). This term, 7F_1 , can be split into three components (Fig. 5), and it would be expected that the 300, 390, and

430 cm^{-1} levels are these components. However, this assumption seems to lead to poor agreement with the observed magnetic susceptibilities, while the assumption of a single term at 300 cm^{-1} , such as would be found with the ion in a cubic field, leads to relatively good agreement, as shown by Table 11.

TABLE 11
MAGNETIC SUSCEPTIBILITY OF EUROPIUM IN $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

$T^\circ \text{K}$	Experimental ¹	$\mu_{\text{eff.}}$ in Bohr Magnetons	
		Calculated ² 300 cm^{-1}	Calculated ² 300, 385, 420 cm^{-1}
83	2.06	2.13	1.94
153	2.73	2.81	2.59
223	3.14	3.16	2.97
293	3.41	3.39	3.22
343	3.58	3.53	3.34

¹ The experimental data are from Selwood [*J. Am. Chem. Soc.*, **55**, 4869 (1933)]. Other values at 293° K for the same compound are 3.63 [Hughes and Pearce, *J. Am. Chem. Soc.*, **55**, 3277 (1933)] and 3.61 [Cabrera and Duperier, *Compt. rend.*, **188**, 1640 (1929)].

² Spedding, Moss, and Waller [*J. Chem. Phys.*, **8**, 908 (1940)]; the authors note that the calculation is made on a shaky theoretical basis. Compare Frank [*Phys. Rev.*, **48**, 765 (1935)], who reports that splitting due to a rhombic field would not affect the agreement found with an assumed cubic field. It is clear that neither the experimental results nor the theoretical interpretations are in a satisfactory state.

In samarium and possibly europium more levels are found than are expected from the theory. These discrepancies seem more serious than not finding enough levels because it is always possible that transitions from some levels are forbidden or are of weak intensity. Ions in which too few levels appear to be found are praseodymium, neodymium, erbium, and dysprosium; all were examined in the octahydrated sulfate. The spectroscopically observed levels can be interpreted nicely by assuming a cubic field about the ion. By choosing the field strength so that the proper over-all spacing of the neodymium levels is obtained, the levels of all the ions can be calculated without evaluating further parameters [Penny and Schlapp, *Phys. Rev.*, **41**, 194 (1932); Penny and Kynch, *Proc. Roy. Soc. London*, **A170**, 112 (1939)]. The results, as seen in Table 12, show good agreement with experiment.

Unfortunately the agreement between calculated and observed values does not extend to other physical properties, which seem to demand a less symmetrical field and consequently more levels. Krish-

man and Mookherji [*Phil. Trans.*, **A237**, 135 (1938)] have found a 10% magnetic anisotropy in the compounds which is incompatible with a cubic field. Penny and Kynch show that the calculated and observed values for the magnetic susceptibility of neodymium fail to agree at low temperatures. In addition, Kynch [*Trans. Faraday Soc.*, **33**, 1402

TABLE 12

OBSERVED AND CALCULATED ELECTRONIC LEVELS

Tripositive		Ground Term	Component Levels, cm ⁻¹
Ion			
Pr ⁺⁺⁺		³ H ₄	Obs. ¹ 0, 110, 235, 500 Calc. 0, 121, 207, 467
Nd ⁺⁺⁺		⁴ I _{9/2}	Obs. ² 0, 77, 260 Calc. 0, 76, 260
Er ⁺⁺⁺		⁴ I _{15/2}	Obs. ³ 0, 19, 41, 85 Calc. 0, 19, 38, 85, 89
Dy ⁺⁺⁺		⁶ H _{15/2}	Obs. ⁴ 0, 22, 57, 80, 112 Calc. 0, 53, 57, 84, 107

¹ Spedding, Howe, and Keller, *J. Chem. Phys.*, **5**, 416 (1937).

² Spedding, Hamlin, and Nutting, *J. Chem. Phys.*, **5**, 191 (1937).

³ Mehan and Nutting, *J. Chem. Phys.*, **7**, 1002 (1939).

⁴ Spedding, *J. Chem. Phys.*, **5**, 316 (1937).

(1937)] has shown that, if the theoretical calculations are refined by considering more carefully the structure of the crystals, the field may not be taken as simple cubic and the agreement shown in Table 12 is lost. It may be concluded that no theory has yet been advanced which can reconcile all the observed physical properties of the rare-earth compounds.

The discussion up to this point has dealt mainly with the absorption spectra. Other data which should aid greatly in the solution of the problem of the electronic levels come from the fluorescent spectra of the rare earths. Samarium, europium, terbium, and dysprosium give visible fluorescent light; cerium, gadolinium, erbium, and possibly others fluoresce in the ultraviolet. It has been suggested that the fluorescence of the mineral fluorite is due to traces of europium acted upon by small amounts of radioactive substances. Pure europium dichloride shows a broad band in the blue identical with the fluorite band [Przilram, *Nature*, **135**, 100 (1935)].

The detailed interpretation of the fluorescent spectra involves the same problems as the analysis of the absorption spectra. Although a number of investigations have been made and several term schemes proposed, the conclusions are still in considerable doubt. The following

references give a survey of the work to date: Gobrecht, *Ann. Physik*, **31**, 600 (1938); Tomaschek and Deutschbein, *Physik. Z.*, **34**, 374 (1933); and Chatterjee, *Z. Physik.*, **113**, 96 (1939).

Until the electronic levels are better understood, there is considerable difficulty in correlating the observed weak satellite lines, either sharp or diffuse, with the various vibrational levels of the crystal. The nature of these lines is, however, clearly shown by the work of Ewald [*Ann. Physik.*, **34**, 209 (1939)], who studied a number of neodymium salts. Ewald found that the separation of many weak, sharp lines from the strong lines corresponded well to the known Raman frequencies for the negative radical in the crystal. This correspondence is shown in Table 13.

TABLE 13

RAMAN FREQUENCIES OF NEGATIVE RADICALS AS FOUND IN THE ABSORPTION SPECTRA OF NEODYMIUM SALTS

Compound	Radical	$\Delta\nu_{\text{obs.}}$	$\Delta\nu_{\text{Raman}}$
$\text{Zn}_2\text{Nd}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	NO_3^-	716	725
$\text{Mg}_3\text{Nd}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$		746	
		1046	1055
		1051	
		1310	1370
$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	NO_3^-	709	725
		746	
		1034	1055
		1045	
		1294	1370
$\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	SO_4^-	995	990
		1011	
		1120	1125
		1342?
$\text{NdBr}_3 \cdot 6\text{H}_2\text{O}$	H_2O	1640	1615
		1199	1220
	D_2O	1431	1460
$\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$	H_2O	1640	1615
		1238	1220
	D_2O	1481	1460

The excellent agreement makes the interpretation most probable. It is puzzling, however, why such agreement has not been found for

other elements even when it was looked for; Spedding [*J. Chem. Phys.*, **8**, 908 (1940)] could find no sulfate frequencies in the europium sulfate spectrum, for example.

Ewald also made the observation that the weak, diffuse lines which extend to a distance of some 500 to 700 cm^{-1} on the violet side of the sharp, strong groups are probably lattice vibrations, as the replacement of light by heavy water or of magnesium by zinc resulted in a displacement of the diffuse lines toward the red. This interpretation has been confirmed by the reststrahlen measurements of Hellwege [*Z. Physik*, **113**, 192 (1939)]. These results of Ewald have a direct bearing upon the theory of crystals. A study of the diffuse bands from the lattice vibrations should give an idea of their frequency distribution, which is of importance in many calculations, such as that of the specific heat.

A further application of the absorption spectra of the rare-earth ions is in the interpretation of the structure of solutions. The same information as to the strength and symmetry of the fields about the ions can be derived as with crystals. Not all the rare-earth ions give sufficiently sharp lines to be resolved at room temperature, but europium has been found satisfactory. The work has been done largely by Simon Freed and his co-workers [*Rev. Modern Phys.*, **14**, 105 (1942); *J. Chem. Phys.*, **7**, 824 (1939), and earlier papers]. A summary of representative data is given in Table 14.

TABLE 14

LINES IN $J = 0$ TO $J = 3$ TRANSITION OF TRIPOSITIVE EUROPIUM ION IN SOLUTION

Solution	Lines in Group at 4650 Å $J = 0 \rightarrow J = 3$
EuCl ₃ in water 1.5-0.0007 <i>M</i>	4640, 4645, 4649, 4658 Å "Chloride quartet"
Eu(NO ₃) ₃ in water 1.5-0.01 <i>M</i>	4644, 4648, 4654 Å "Nitrate triplet"
Eu(NO ₃) ₃ in water 0.01-0.0007 <i>M</i>	Gradual appearance of chloride quartet and disappearance of nitrate triplet
EuCl ₃ + KNO ₃ in water ~0.003 <i>M</i> in Cl ⁻ and NO ₃ ⁻	Mainly nitrate triplet, very faint chloride quartet
Eu(NO ₃) ₃ in anhydrous ether	Two strong lines
EuCl ₃ in anhydrous alcohol	4641, 4650, 4662.5 Å
EuCl ₃ in 90% alcohol-10% water	Chloride quartet alone
Eu(NO ₃) ₃ in anhydrous alcohol	4650.3, 4658.6, 4660.7 Å
Eu(NO ₃) ₃ in 75% alcohol-25% water	Nitrate triplet alone

No detailed interpretation of the data is yet possible. Less polar solvents seem to give a field of higher symmetry about an ion; europic

nitrate in ether gives two lines in the group, in alcohol two lines close together and one farther off, and in water three almost equally spaced lines. The field about a positive ion depends upon the negative ion present, as would be predicted by the Debye-Hückel theory. The sharpness of the lines points to a relatively stable configuration about an ion.

A further point of interest not shown in the table is that diffuse satellite lines were observed that were remarkably similar to those from crystals [Freed and Weissman, *J. Chem. Phys.*, **8**, 840 (1940)]. This indicates a definite regularity in the structure of a solution, possibly a greater regularity than is now believed to exist.

The coordination compound europic acetylacetonate, $\text{Eu}(\text{OCCH}_3\text{-CHC}(\text{CH}_3)\text{O})_3$, has also been examined [Freed, Weissman, and Fortress, *J. Am. Chem. Soc.*, **63**, 1079 (1941)] with the results indicated in Table 15.

TABLE 15

ABSORPTION SPECTRA OF EUROPIAC ACETYLACETONATE

Substance	Lines in Blue	Lines in Yellow
	$J = 0 \rightarrow J = 3$	$J = 0 \rightarrow J = 0$
Crystalline europic acetylacetonate	five	one
	monomer	
Europic acetylacetonate in benzene or carbon tetrachloride	4667.6 Å	
	4663.3	5794.3 Å
	4658.7	5796.5
	4651.1	
	4649.8	
	4644.9	
	dimer	
	4665.3 Å	
	4655.1	
	4651.1	5778
	4644.9	5782
	4639.9	
	4636.7	

For the transition $J = 0$ to $J = 3$ a maximum of seven lines is possible; for $J = 0$ to $J = 0$ only one line is possible. In order to account for the large number of lines observed (especially the four in the yellow) it seems necessary to postulate four distinct kinds of tripositive europium ion. Two kinds are readily accounted for by an equilibrium between a monomer and dimer. The crystal dissolves to give mainly dimer and requires several weeks to reach equilibrium; the shifting intensities of the lines made it possible to assign them to either the

monomer or dimer. This assumption still leaves two species unaccounted for. Freed, Weissman, and Fortress postulated that both the monomer and dimer exist in two isomeric forms. The two isomers of the dimer might be the optically active and inactive forms, but isomerism of the monomer would be of a kind as yet unsuspected. The possibility warrants further investigation.

Chapter 4

EVIDENCE FOR THE EXISTENCE OF ELEMENT 61

Almost nothing has been said about element 61 up to this point. Attempts have been made to isolate this element ever since the work of Moseley demonstrated that an element with this atomic number should exist between neodymium and samarium in the periodic table. From the first it has been thought by most investigators to be a member of the rare earths, and methods of isolating it have been based in general on this assumption.

In 1917 Eder [*Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, IIa*, 125 (1917)] photographed the arc spectrum of a samarium preparation and found lines that he believed indicated the existence of the new element. Hadding [*Z. anorg. allgem. Chem.*, **122**, 195 (1922)], five years later, came to a similar conclusion after studying the X-ray spectrum of fluocerite, a basic fluoride of the cerium earths. An investigation of the rates of hydrolysis of some rare-earth carbonates also seemed to indicate an element existing between neodymium and samarium [Brinton and James, *J. Am. Chem. Soc.*, **43**, 1446 (1921)]. An examination by Prandtl and Grimm [*Z. anorg. allgem. Chem.*, **136**, 283 (1924)] of the X-ray spectra of some fifty preparations resulting from exhaustive fractionation of the cerium earths gave no indication of element 61, however; they suggested that this element might be a homolog of manganese rather than a rare earth. With this in mind, Druce and Loring [*Chem. News*, **131**, 273 (1925)] studied the X-ray spectrum of a concentrate from manganese preparations but failed to find anything new.

In 1926 the discovery of the new element was claimed to have been made by Harris, Yntema, and Hopkins [*J. Am. Chem. Soc.*, **48**, 1585, 1594 (1926); *Nature*, **117**, 792 (1926); *Science*, **63**, 575 (1926)]. They named the element "illinium" (in honor of the University of Illinois where their work was carried out) and presented the following evidence for its existence: (1) the presence of 130 lines in the red and infrared, and 5 lines toward the violet common to the arc spectra of neodymium and samarium preparations, these lines becoming more intense in the intermediate fractions where element 61 was expected to concentrate; (2) the occurrence of new absorption bands in solutions obtained from

the intermediate fractions, these bands becoming stronger as the characteristic bands of neodymium and samarium became weaker; (3) an examination of the X-ray emission spectra of intermediate fractions revealing lines corresponding closely with the theoretical positions for $L\alpha_1$ and $L\beta_2$ of element 61, the maximum deviation from the theoretical wavelength being less than 0.005 \AA . With regard to the last piece of evidence they stated that possibilities of lines arising from other elements in the first, second, and third orders, or by defects in the crystals, could be regarded as negligible. However, Prandtl [*Z. angew. Chem.*, **39**, 897, 1333 (1926)] criticized this point and stated that the lines in the X-ray spectra were probably due to small amounts of barium, bromine, and platinum.

Immediately after publication of the work of Harris, Yntema, and Hopkins other papers on element 61 appeared. Some German workers [Meyer, Schumacher, and Kotowski, *Naturwissenschaften*, **14**, 771 (1926); Dehlinger, Glocker, and Kaupp, *Naturwissenschaften*, **14**, 772 (1926)] reported that they had obtained the K series lines of element 61 on a sample of rare-earth materials. K series lines of element 61 were also said to have been found and measured by James, Cork, and Fogg [*Proc. Natl. Acad. Sci.*, **12**, 696 (1926)], who used a neodymium concentrate prepared from three separate sources. Rolla and Fernandes [*Gazz. chim. ital.*, **56**, 435 (1926); **56**, 862 (1926); *Z. anorg. allgem. Chem.*, **157**, 371 (1926); *Nature*, **119**, 637 (1927)] claimed that they had already discovered element 61 as the result of X-ray and absorption spectra work carried out at the University of Florence. They insisted that the new element should be called "florenziun" and claimed that Rolla had placed a sealed record of the work in a vault of the Academy of Lincei in 1924. The careful work of Noddack [*Angew. Chem.*, **47**, 301 (1934)] on the X-ray spectra of so-called illinium concentrates, and the work of a number of other investigators, gave negative results, however.

Arguments against the existence of element 61 in nature have been based on nuclear stability considerations [e.g., see the paper of Segrè, *Scientific Monthly*, **57**, 12 (1943)]. The rules of isotopic statistics [e.g., Aston, *Mass Spectra and Isotopes*, Longmans, Green and Co., New York, 1933; Mattauch, *Z. Physik*, **91**, 361 (1934)], especially (1) the trend of the isotopic number, I , with atomic number ($I = A - 2Z$, where Z is the atomic number and A is the atomic mass number, i.e., the integer nearest to the atomic weight; I is thus the difference between the number of neutrons and the number of protons comprising a nucleus), (2) the odd-even rule, i.e., the rule that there are no stable nuclei of odd Z greater than 7 with even A , and (3) the isobar rule that pairs of stable neighboring isobars should not exist, result in the pre-

diction that there are no stable isotopes of element 61 when consideration is given to the known stable isotopes of neodymium (No. 60) and samarium (No. 62). These rules are based upon extensive empirical data and have reasonable theoretical interpretation; however, three apparent exceptions to the isobar rule are known at present, one of each of the three pairs of neighboring isobars involved presumably being radioactive with a very long half-life. The possibility of an unstable isotope of element 61 existing in nature due to a half-life comparable with or longer than the age of the earth has not been ruled out, therefore.

The problem of the isolation of this element is one which definitely deserves further investigation. Although Harris, Yntema, and Hopkins deserve much credit for their work on element 61, the nature of the evidence for the existence in nature of element 61 is somewhat circumstantial rather than conclusive, and the isolation of this element cannot be regarded as having been effected.

Mention should be made here that some evidence exists for the formation of radioactive isotopes of element 61 in the deuteron, proton, and helium-ion bombardments of certain rare-earth preparations (see Appendix 1). However, the assignments of the activities in question appear very uncertain. The assignment of a beta activity of four-year half-life in one of the chains from uranium fission to element 61, mass number 147, has been announced by workers on the Manhattan project [*Science*, **103**, 697 (1946)].

Chapter 5

SEPARATION OF THE RARE EARTHS

Occurrence and Relative Abundance of the Rare Earths. Since the term "rare earths" implies some scarcity of these elements, it is of interest to consider the relative abundance of each one. Table 16 gives the average weight percentage of each element in the rare-earth content of all known rare-earth ores, and also the percentage of each one in the earth's lithosphere (based on an estimate that the group constitutes about 0.005% of the crust). The members with even atomic numbers are more abundant than their odd-atomic-numbered neighbors. Cerium makes up nearly one-third of the whole group,* and it has found more commercial applications than the other members.†

The principal source of the rare earths is the mineral monazite, found as an alluvial sand in Brazil, India, and Idaho. This is essentially a complex phosphate, containing often as much as 70% cerium. Other important mineral sources are gadolinite (a silicate, found in Norway, Sweden, Colorado, and Texas), fergusonite (a columbate and tantalate, found in Norway, Texas, and Australia), samarskite (a tantalate and uranate, found in the Urals and North Carolina), xenotime (a phosphate, found in Brazil and Norway), yttrocerite (a fluoride, found in Scandinavia), cerite (a basic silicate, found in Sweden), and allanite

* Cerium is more abundant than such "common" elements as tin, mercury, cadmium, antimony, bismuth, and tungsten.

† The pyrophoric properties of cerium alloys have made them of some use in the removal of oxygen from cast iron, in tracer bullets and luminescent shells which show their path by the light evolved on ignition of the alloy, and in cigarette and gas lighters. Cerium dioxide is used as a fine abrasive for polishing glass and soft metals. Its greatest use is in the manufacture of gas mantles, which are approximately 99% thoria and 1% ceria. Although gas mantles do not seem so important today, Levy wrote in 1915 (*The Rare Earths*, Longmans, Green and Co., New York, 1915), "During the thirty years which have elapsed since Dr. Auer's application of the rare earths to the production of artificial light, the incandescent mantle industry has developed to an extent which gives it a prominent place among those chemical industries which may be considered essential to modern civilization."

A large part of the work on rare earths has been aided by the mantle industry either through the earlier direct support or in more recent times through the supply of concentrates of rare-earth salts. Ceric salts are often used as oxidizing agents. Among the applications of other rare earths are the use of lanthanum sesquioxide in optical glass, the well-known didymium mixture for glassblowers' goggles, and mixed rare-earth fluorides and oxides for "core mixture" in cored graphite rods for searchlights.

TABLE 16
RELATIVE ABUNDANCE OF THE RARE EARTHS

Rare Earth	Percentage of Group	Percentage of Earth's Crust
La 57	7	0.00035
Ce 58	31	0.00155
Pr 59	5	0.00025
Nd 60	18	0.00090
61	(?)	(?)
Sm 62	7	0.00035
Eu 63	0.2	0.00001
Gd 64	7	0.00035
Tb 65	1	0.00005
Dy 66	7	0.00035
Ho 67	1	0.00005
Er 68	6	0.00030
Tm 69	1	0.00005
Yb 70	7	0.00035
Lu 71	1.5	0.00007

(a silicate, found in Greenland and Scandinavia). The method selected for the extraction of the rare earths from the ore depends on the nature of the ore and the presence of other elements. (For discussions of this problem see Levy, *The Rare Earths*; Spencer, *The Metals of the Rare Earths*; Böhm, *Darstellung der seltenen Erden*, Vol. I.)

It may be of some interest to mention that it has been shown recently that all the rare earths except element 61, holmium, terbium, and lutecium are present in small amounts in a number of plants.

Separation of the Rare-Earth Elements. The great similarity in chemical properties of the rare-earth elements has made their separation a problem of extraordinary difficulty. The procedure most utilized has been fractional crystallization; only in recent years has this tedious method been improved upon by the introduction of separations depending upon the oxidation or reduction of some of the elements to other than the tripositive state. As further research on this unique group in many branches of chemistry and physics is greatly impeded by the scarcity of pure compounds, it is of considerable importance that any promising method of separation be fully utilized.

In discussing the rare earths * it is convenient to divide them into

* Although scandium and yttrium are not in the rare-earth group, they always occur in considerable quantities in the rare-earth minerals and have to be considered in all separations. Fortunately, scandium is distinguished by its greater complex-forming power and can be removed by precipitating the rare-earth fluorides in strong ammonium bifluoride solution. The scandium forms a soluble complex fluoride ion and stays in solution. The behavior of the yttrium is so like that of the rare-earth elements that more tedious methods are required for its separation.

two groups—the cerium group and the yttrium group. The cerium group includes the elements La, Ce, Pr, Nd, Sm, and Eu; the yttrium group includes Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. The division is by no means sharp, and europium is often included in the yttrium group. The groups are named for the element occurring in the greatest amount in the principal ores. Reasons for the division will be apparent when the separations are considered.

The initial material for the preparation of the cerium group is almost always thorium-free residues from monazite sands obtained from plants engaged in separating thorium commercially. The starting material for the yttrium group is either the residues of minerals which have these elements in greater proportion such as xenotime or the more soluble fraction left after the separation of the cerium group from the monazite sands residue.

The elements are generally present in proportion to their abundance in the earth's crust. The amount of starting material depends accordingly upon which element is desired, the quantity needed, and the degree of purity desired. Only Ce, Eu, and Yb can be recovered approximately quantitatively in a high degree of purity. The salts of the more abundant La, Pr, Nd, Sm, Gd, Dy, and Y are much easier to prepare than salts of the much less abundant Tb, Ho, Er, and Tm; poor yields are invariably obtained. The elements holmium and erbium must not only be separated from the neighboring elements but also from yttrium which follows them very tenaciously. Since lanthanum and lutecium come at the ends of the series and consequently have a rare-earth neighbor on only one side, their separation in fair yields is relatively easy.

Fractional crystallization is utilized at some time in the separation of any rare earth. In order to give a quantitative idea of the variations in solubility upon which the method depends, the solubilities of some salts which have been extensively used in separations are given in Table 17 [sulfate, Jackson and Rienacker, *J. Chem. Soc.*, 1930, 1687; bromate, James and others, *J. Am. Chem. Soc.*, 49, 132 (1927); phosphate, Marsh, *J. Chem. Soc.*, 1939, 554; nitrate, Jantsch, *Z. anorg. Chem.*, 76, 321 (1912)].

In practice the total solubility and the nature of the precipitate formed are important as well as the variation in solubility from one element to the next. The magnesium double nitrate is used especially for the separation of the cerium group; the bromate and dimethyl phosphate are used for the separation of the yttrium group. It is interesting to note that the dimethyl phosphates are the only known salts of the rare-earth metals that fall steadily in solubility from lanthanum to lutecium.

TABLE 17
SOLUBILITIES OF SOME RARE-EARTH COMPOUNDS

	$R_2(SO_4)_3 \cdot 8H_2O$ g/100 g H_2O		$R(BrO_3)_3 \cdot 9H_2O$ g/100 g H_2O		Dimethyl phosphate g/100 g H_2O			$2R(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$ g/100 g sat. soln. in conc. HNO_3 $d_{4^{\circ}}^{16^{\circ}} = 1.325$
	20° C	40° C	25° C	35° C	0° C	25° C	50° C	16° C
La(-9H ₂ O)	2.2 ¹		462.1	1061.5		103.7		6.38
Ce	9.43 ¹	5.70 ¹				79.6		5.85
Pr	12.74	7.64	196.1	278.5				7.70
Nd	7.00	4.51	151.3	205.8		56.1		9.77
Sm	2.67	1.99	117.3	157.2		35.2		24.55
Eu	2.56	1.93						
Gd	2.89	2.19	110.5	144.5	37.0	24.2	15.7	35.23
Tb	3.56	2.51	133.2	172.9	24.2	12.6	8.07	
Dy	5.07	3.34			15.0	8.24	4.83	
Ho	8.18	4.52						
Y	9.76	4.90			6.44	3.53	1.90	
Er	16.00	6.53			6.91	3.36	2.03	
Yb	34.78	22.9			2.68	1.35	0.72	
Lu	47.27	16.93						

¹ Grams anhydrous salt/100 g H_2O .

A major difficulty in working with the rare earths is the scarcity and cost of the starting materials. The constituents desired make up only a small portion of the minerals in which they occur, and all fractions must be hoarded carefully. The system of fractional crystallization worked out to achieve this is illustrated in Fig. 7.

An idea of the effectiveness of a single crystallization is given by the data of Selwood [*J. Am. Chem. Soc.*, **55**, 4900 (1933)] for a number of

TABLE 18
LANTHANUM-NEODYMIUM SEPARATIONS

Method	Precipitate g Oxide	% Nd in Precipitate	% Nd in Filtrate	More Soluble Element
Sulfate	2.9	24	35	Nd
Oxalate	3.1	43	16	La
Alkali carbonate	5.3	25	62	Nd
NH_4 double nitrate	3.5	20	44	Nd
Basic magnesia	1.2	61	22	La
Basic ammonia	2.3	59	11	La
Basic urea	1.9	43	23	La
Basic electrolytic	1.0	60	24	La

different separations in the favorable case of lanthanum and neodymium (Table 18). Fractions were analyzed by their magnetic susceptibilities. The original mixture contained 29.6% neodymium.

Identical 6-gram samples of mixed oxides were taken in each experiment.

Even the best separations must be repeated many times to achieve satisfactory purity. It can be imagined what a task it is to separate each of the elements in a pure state. W. Prandtl has summarized in an excellent article [*Z. anorg. allgem. Chem.*, **238**, 321 (1938)] the results of his long experience in purifying the rare-earth elements. Table 19 prepared from his suggestions illustrates most of the procedures that

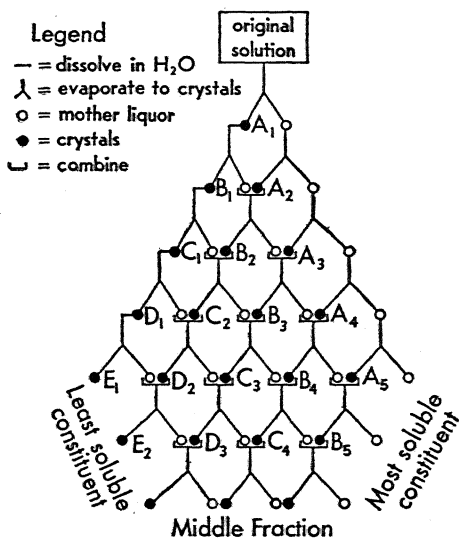


Fig. 7. Diagrammatic representation of the system of fractional crystallization used to separate salts of the rare-earth elements.

have been found especially useful. The tabular outline is not intended to be a complete working procedure, but it presents a clear picture of the difficulties of the process.

The separation of the cerium and yttrium groups can be achieved by several methods, none being completely satisfactory. The precipitation of the basic salts and of the alkali double sulfates in a concentrated solution of sodium sulfate is shown in the tabular outline. In addition the separation may be made with potassium carbonate which precipitates the mixed carbonates of the cerium group. Some neodymium, samarium, and europium usually remain, and these are removed more completely as the formates in an ammonium formate, formic acid solution. The use of sulfamic acid has been proposed instead of sodium sulfate [Kleinberg, Taebel, and Audrieth, *Ind. Eng. Chem., Anal. Ed.*,

TABLE 19
SEPARATION OF THE RARE-EARTH ELEMENTS

<p>Thorium-free residue from monazite sands in Cl^- or NO_3^- solution. Oxidize with NaClO and add NaOH.</p>			
<p>Precipitate: mainly $\text{Ce}(\text{OH})_4$ Dissolve in HNO_3 and H_2O_2 soln. If Nd or Pr absorption bands are present, repeat procedure. Solution: Ce^{+++}. Purify Ce^{+++} by fractional crystallization as magnesium cerous nitrate. Pure Ce</p>	<p>Filtrate: other rare-earth ions. Add NH_3, NH_4NO_3, and $\text{Ce}(\text{NO}_3)_2$: Pr absorption lines.</p>	<p>Filtrate: La^{+++} Ppt. Ce^{+++} with H_2S. Discard ppt. Purify La^{+++} by fractional crystallization as magnesium lanthanum nitrate. Pure La</p>	
	<p>Precipitate: hydroxides of rare earths except Ce and La; Dissolve ppt. in HNO_3. Solution: rare-earth ions except La^{+++} and Ce^{+++}. By additions of NH_3 and NH_4NO_3, precipitate fractionally small amounts of the rare-earth hydroxides.</p>	<p>End fractions: Pr^{+++}, Nd^{+++}, Eu^{+++}, Sm^{+++}, some La^{+++}, and Gd^{+++}. Make magnesium double nitrate fractional crystallizations.</p>	
	<p>Head fractions: colorless ppt. of Lu, Yb hydroxides (Th and Sc appear here if they have not been removed completely). Yttrium group fractions (see below)</p>	<p>Head fractions: green solution of La^{+++}, Pr^{+++}, no Nd^{+++}. Separate La^{+++} by basio precipitation method used above. Pure Pr</p>	<p>Middle fractions: rose solutions of Nd^{+++} and Sm^{+++}. Continue magnesium double nitrate fractional crystallizations. Pure Nd</p>
		<p>End fractions: yellow solutions of Sm^{+++}, Eu^{+++}, some Nd^{+++} and Gd^{+++}. Continue magnesium double nitrate fractional crystallization.</p>	<p>Fractions containing Eu^{+++}, Sm^{+++}, and some Gd^{+++}. Electrolyze sulfate solution.</p>
		<p>Head fraction: Sm^{+++}. Continue magnesium double nitrate crystallization. Pure Sm</p>	<p>Precipitate: EuSO_4, some $\text{Gd}(\text{OH})_2$. Dissolve with HNO_3, and reduce with zinc, and add conc. HCl to precipitate EuCl_2. Pure Eu</p>
			<p>Solution: Sm^{+++}, some Eu^{+++} and Gd^{+++}. Add to samarium fractions.</p>

Yttrium group fractions: Y, Gd, Tb, Dy, Er, Ho, Tm, Yb, Lu, and some cerium group hydroxides. Dissolve each fraction in dilute nitric acid; add powdered Na_2SO_4 to the warm, well-stirred solution until the strong absorption line of Nd is not detectable in the solution.

Precipitate: cerium group sulfates.
Add to previous cerium group samples.

Solutions: yttrium group elements.

Add warm conc. $\text{K}_2\text{Fe}(\text{CN})_6$ solution to the neutral solutions until the absorption lines of Ho and Er have disappeared from the solutions.

Precipitates: ferrioxalides of yttrium group in various fractions. Most of yttrium removed.

Treat precipitates with conc. NaOH solution, add much water, and filter the resulting hydroxides. Dissolve in HNO_3 or HCl, and repeat procedure. Fractionally crystallize the bromates.

Head fractions: Gd^{+++} , Tb^{+++} , some Nd^{+++} , Er^{+++} , and Sm^{+++} .	Middle fractions: Tb^{+++} , some Gd^{+++} and Dy^{+++} .	Middle fractions: Dy^{+++} , some Tb^{+++} , Ho^{+++} , and Y^{+++} .	Middle fractions: Ho^{+++} , Er^{+++} , some Yb^{+++} , and Y^{+++} .	End fractions: Tm^{+++} , Yb^{+++} , La^{+++} , and some Er^{+++} and Ho^{+++} .
A	B	C	D	E

Solution: Y^{+++} .
Add NaOH.

Precipitate: $\text{Y}(\text{OH})_3$.

Dissolve in HNO_3 or HCl and test for absorbing elements (Nd, Ho, Er). Repeat procedure if they are present. Purify yttrium by fractional crystallization of the bromate.

Pure Y

A. Solution: Gd^{+++} , Tb^{+++} , and some Nd^{+++} , Er^{+++} , and Sm^{+++} .
Add powdered Na_2SO_4 as in previous separation of the cerium group. Filter.

Precipitate: $\text{Nd}_2(\text{SO}_4)_3$, $\text{Sm}_2(\text{SO}_4)_3$.
Combine with previous neodymium and samarium fractions.

Solution: Gd^{+++} , Tb^{+++} , some Er^{+++} . Electrolyze sulfate solution.

Precipitate: Eu_2SO_4 .
Combine with previous europium fractions.

Solution: Gd^{+++} , Tb^{+++} . Fractionally crystallize the bromates.

Head fractions: Pure Gd

End fractions: Tb^{+++} .
Combine with other terbium fractions.

B. Solution: Tb^{+++} , some Gd^{+++} and Dy^{+++} .

Fractionally crystallize from hot, weakly ammoniacal concentrated solution of ammonium oxalate.

Head fraction: Gadolinium ammonium oxalate. Combine with previous gadolinium fractions.

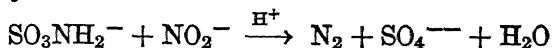
Middle fraction: Tb^{+++} ,
Pure Tb

End fraction: Dy^{+++} .
Combine with other dysprosium fractions.

TABLE 19 (Continued)
SEPARATION OF THE RARE-EARTH ELEMENTS

C. Solution: Dy^{+++} , some Tb^{+++} , Ho^{+++} , Y^{+++} . Fractionally crystallize the bromates.			
Head fractions: Tb^{+++} . Combine with previous terbium fractions.	Middle fractions: Dy^{+++} . Pure Dy	End fractions: Ho^{+++} . Combine with other holmium fractions.	
D. Solution: Ho^{+++} , Er^{+++} , some Y^{+++} and Dy^{+++} . Fractionally crystallize the bromates.			
Head fractions: Dy^{+++} , some Ho^{+++} . Combine with dysprosium fractions.	Middle fraction: Ho^{+++} , some Dy^{+++} , Y^{+++} , and Er^{+++} . Fractionally crystallize the basic nitrates by converting $\frac{1}{4}$ of the salt to the oxide and then dissolving the oxide in a rather conc. nitrate soln. heated to boiling. Cool.		End fractions: Er^{+++} some Y^{+++} and Ho^{+++} . Fractionally crystallize the bromates or the ammo- nium double oxalates. Pure Er
	Head fractions: Y^{+++} . Add to previous yttrium fractions.	Middle fractions: Ho^{+++} . Pure Ho	
E. Solution: Tm^{+++} , Yb^{+++} , La^{+++} , and some Er^{+++} and Ho^{+++} . Fractionally crystallize the ammonium double oxalates as described in B.			
Head fraction: Er^{+++} and Ho^{+++} . Add to erbium and holmium fractions.	Middle fraction: Tm^{+++} . Pure Tm		End fractions: La^{+++} . Pure La
	Middle fractions: Yb^{+++} , Tm^{+++} , La^{+++} . Electrolyze the sulfate solution.		
Precipitate: $YbSO_4$ traces of Tm^{+++} and La^{+++} . Purify by repeated electrolysis or by ammonium double oxalate frac- tional crystallization. Pure Yb		Head fraction: Tm^{+++} . Add to other thulium frac- tions.	End fraction: La^{+++} . Add to other lutetium frac- tions.

11, 368 (1939)]. Oxidation of sulfamic acid with sodium nitrite gives the necessary sulfate ion:



Less material is required, and good separations are obtained. From a sample of mean atomic weight 141.8, a soluble fraction of atomic weight 104.3 and an insoluble fraction of atomic weight 142.3 were obtained.

Other promising methods for various purifications have been developed. Fractional crystallization of the dimethyl phosphates makes the difficult separations of gadolinium, terbium, dysprosium, and holmium much easier than by previous methods (Marsh, *J. Chem. Soc.*, **1939**, 554). Solutions must be kept below 50°, as the salt hydrolyzes at higher temperatures. Appleton and Selwood [*J. Am. Chem. Soc.*, **63**, 2029 (1941)] have found that the distribution ratio between *n*-butyl alcohol and water is different for neodymium and lanthanum thiocyanates. The ratio of neodymium to lanthanum in the alcohol layer is 1.06. This method has promise as it lends itself to continuous operation in an automatic extraction apparatus. The fractional thermal decomposition of various compounds has often been tried for separations. The decomposition of the nitrates is useful for separating yttrium from erbium and ytterbium from lutecium [Boss and Hopkins, *J. Am. Chem. Soc.*, **50**, 298 (1928)]. Brauner [*Collection Czechoslov. Chem. Commun.*, **5**, 279 (1933)] has separated praseodymium from lanthanum by fusion of a mixture of alkali and rare-earth nitrates to a high temperature. The praseodymium is oxidized to a higher oxide which is insoluble. The more soluble lanthanum sesquioxide is washed out of the melt with a concentrated ammonium nitrate solution. Marsh [*J. Chem. Soc.*, **1946**, 17, 19] has also studied separations achieved with nitrate fusions as well as with potassium hydroxide fusions.

Young, Arch, and Shyne [*J. Am. Chem. Soc.*, **63**, 957 (1941)] have found that the soluble anhydrous bromides of rare-earth elements react with ethyl benzoate at 154° to give ethyl bromide and the insoluble rare-earth benzoate. Since the rates differ for the different rare earths, this reaction affords a means of separation. From nearly equimolar mixtures of neodymium and lanthanum bromides, one-quarter of the neodymium is obtained in a degree of purity of 95% in one operation since the neodymium bromide reacts at a faster rate.

Methods of fractionation usually employed for the separation of the individual members of the rare earths are especially unsatisfactory for separating thulium, ytterbium, and lutecium because these elements are very scarce and their trivalent salts tend to be more soluble than the remainder of the rare-earth salts. Hence, these elements generally

accumulate in the most soluble fraction. If this fraction is now subjected to electrolytic reduction, substantially all the ytterbium (the intermediate element in this group of three) can be removed as dispositive ytterbium, and the differences between thulium and lutecium salts will be made more effective for separating them. The separation may be improved by the addition of pure ytterbium, if available, and repeated fractional crystallization until the central fraction is substantially free from thulium and lutecium.

Oxidation and reduction are very effective to achieve separations for cerium, europium, and ytterbium but methods have not been developed for the other elements to any extent. If proper conditions for the oxidation or reduction of the other elements could be found, it would become much easier to obtain pure elements.

If radiochemically pure radioisotopes of the rare earths become available in reasonable amounts for tracer purposes, they will have obvious application to the problems of rare-earth separations.

Analysis of the Rare-Earth Elements. Because of their chemical similarity, the customary methods of quantitative analysis for members of the rare-earth group are useless. All accurate analysis must therefore be based on the physical properties of the elements. The five general criteria available are the average atomic weight, the magnetic susceptibility, the absorption spectra, the X-ray spectrum, and the arc spectrum. Radiochemical methods may prove useful eventually when adequate tracer radioisotopes are generally available. The average-atomic-weight method is extremely useful in following separations as no special equipment is required. The usual practice is to find the oxide-oxalate ratio and to determine the oxalate by permanganate titration.

The development of the mass spectrograph for the highly accurate determination of the masses of the individual isotopes and their relative abundance has made the chemically determined atomic weight a highly accurate criterion for absolute purity. This is well illustrated by holmium. The chemical atomic weight was determined by Holmberg in 1910 to be 163.5 [*Z. anorg. Chem.*, **71**, 268 (1911)], and this value was confirmed in 1925 by Driggs and Hopkins [*J. Am. Chem. Soc.*, **47**, 363 (1925)] on different material, analyzed by magnetic-susceptibility measurements. Accordingly the value 163.5 was accepted until Aston [*Proc. Roy. Soc. London*, **A146**, 46 (1934)] found that holmium consists of the single isotope 165 and that its atomic weight is 164.95; the samples for the chemical determination must have contained some dysprosium or yttrium. Hönigschmid and Hirschbold-Wittner have since redetermined the chemical atomic weight and obtained the value 164.94 in agreement with the mass-spectrograph value [*Z. anorg. allgem.*

Chem., **244**, 63 (1940)]. The exact agreement on an incorrect value by two investigators in different countries using different methods on material purified in different ways was a most striking coincidence. At present two discrepancies remain, both for elements with a single isotope:

	CHEMICAL ATOMIC WEIGHT	MASS-SPECTROGRAPH ATOMIC WEIGHT
Terbium	159.2	158.93
Thulium	169.4	168.95

The use of the magnetic susceptibility as a criterion for purity has the drawback of requiring special equipment, but has the great advantage that it is quick and does not require that the sample be converted to any particular form. It is especially useful for following the course of the separation of a paramagnetic element from a diamagnetic one. The sensitivity, however, is not comparable with that of the spectroscopic methods.

Since many of the rare earths are colored, the visual examination of the absorption spectrum is a most convenient method of analysis. Its drawbacks are that several of the rare earths are colorless and the bands of others overlap. This method is of great practical use but even in the best cases is hardly sufficient as the final test of purity although about 0.1% of a highly colored element can be detected.

The two remaining spectroscopic methods of analysis are of extreme sensitivity, and they are the final criteria for the purity of a rare-earth sample. Both require special equipment and considerable skill in their application. The arc spectra will be of more and more use as the difficult problem of classifying the almost countless lines of the various elements progresses. Until now the most certain method of analysis has taken advantage of the well-defined X-ray spectra. The sensitivity of the method is illustrated by the report on the holmium used in the atomic-weight determination by Hönigschmid. Noddack found 0.013 ± 0.004 atomic per cent of yttrium, 0.04 atomic per cent of erbium, 0.03 atomic per cent of dysprosium, and a maximum of 0.02 atomic per cent of other rare-earth elements.

In addition to the general analytical methods some specific tests are of great value. A sensitive test for cerous ion is to precipitate the salt with ammonia and then to add hydrogen peroxide. A reddening of the precipitate due to the formation of cerous peroxide shows the presence of cerium. Praseodymium in lanthanum, cerium, or neodymium gives a brown or gray tint to the oxides. This test is sensitive to about 1%. A similar test exists for terbium in gadolinium. One-tenth per cent of

samarium in neodymium, europium, or gadolinium can be detected by heating an anhydrous halide at about 700° C in a hydrogen atmosphere; the halide will be colored brown by the bivalent samarium. Europium and ytterbium can be tested for by electrolysis in sulfuric acid solution. Several per cent must be present before a precipitate can be observed. The test is better for ytterbium because the green color of the ytterbous ion can be detected before a precipitate forms. The presence of gadolinium in a sample might be inferred if the sample were found to have a high absorption of thermal neutrons, although certain other elements also have very large capture cross sections for thermal neutrons (see Appendix 1 for nuclear properties of the rare earths).

Chapter 6

CHEMICAL AND PHYSICAL PROPERTIES OF THE RARE EARTHS

Preparation and Properties of the Rare-Earth Metals and Compounds. Because of the relatively great difficulty in separating the chemically similar rare earths from one another by the customary methods of fractional crystallization, a large body of qualitative chemical knowledge has been obtained about rare-earth compounds in the hope that easier methods of separation might be discovered. Little is known about most rare-earth compounds from a quantitative standpoint. In the present discussion attention will be paid mainly to the well-known compounds of the rare earths in non-trivalent states and to those that are fundamental to a proper understanding of the chemistry of the whole group.*

All the cerium metals (La, Ce, Pr, Nd, Sm) have been prepared, most of them in a somewhat impure state.† Methods for their preparation include: (1) the reduction of the oxide or halide by means of an alkali metal (usually sodium), calcium, or magnesium, a method which often results in the formation of an alloy; (2) the electrolysis of the fused halide, usually the anhydrous chloride; and (3) the preparation of an amalgam by reduction of an alcoholic solution of the proper salt with a mercury cathode, followed by removal of the mercury by distillation in a vacuum. Since the metals are easily oxidized in air and readily form silicides, ordinary glass and porcelain vessels cannot be used in their preparation; crucibles made of purified magnesia are suitable for this purpose, and a layer of barium chloride serves to exclude air.

With the exception of europium, the yttrium metals (Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) have not been isolated in any form remotely approaching the pure metal, because they have melting points much

* For a more complete treatment of the different compounds, see such works as J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. V, Longmans, Green and Co., London, 1924; J. N. Friend, *A Textbook of Inorganic Chemistry*, Vol. IV, Charles Griffin and Co., London, 1921; Gmelin-Kraut, *Handbuch der anorganischen Chemie*, Vol. VI, parts 1 and 2, Heidelberg, 1928 and 1932; and Abegg, *Handbuch der anorganischen Chemie*, Vol. III, part 1, Leipzig, 1906.

† The preparation of 99.8% La, 99.8% Ce, and 99.6% Ce has been reported [Weibke, *Z. Electrochem.*, **45**, 518 (1939); Bommer and Hohmann, *Z. anorg. allgem. Chem.*, **241**, 268 (1939)].

higher than the cerium metals and because their halides are more volatile; both properties make the electrolytic method, which is otherwise the most suitable, more difficult to carry out. Trombe [*Compt. rend.*, **206**, 1380 (1938)] has succeeded in preparing 98% pure europium (impurities are Cd, Si, and Fe) by the electrolysis of a fused mixture of europium trichloride with a eutectic melt of sodium chloride and potassium chloride at 700° C, using a graphite anode and a cadmium cathode. The metallic europium so prepared is steel gray and is malleable. Yttrium, which is not one of the rare earths, although it lends its name to this group of rare earths for historical reasons, has also been obtained in an impure metallic state.

It is noteworthy that a small sample (0.12 g) of nearly pure (99.27%) metallic gadolinium has been prepared by Trombe [*Compt. rend.*, **200**,

TABLE 20
STRUCTURES OF THE RARE-EARTH METALS

h.c.p. is hexagonal closest-packing; c.c.p. is cubic closest-packing; and c.b.c. is cubic body-centered

		a	c	Atomic Radius	Density
α -La	h.c.p.	3.754 Å	6.063 Å	1.870 Å	6.194 g/cc
β -La	c.c.p.	5.294		1.872	6.180
α -Ce	h.c.p.	3.65	5.96	1.81	6.78
β -Ce	c.c.p.	5.140		1.817	6.810
α -Pr ¹	h.c.p.	3.662	5.908	1.824	6.776
β -Pr	c.c.p.	5.151		1.821	6.805
α -Nd ¹	h.c.p.	3.650	5.890	1.818	7.004
Sm					6.93
Eu	c.b.c.	4.573		2.042	5.244
Gd	h.c.p.	3.622	5.748	1.794	7.948
Tb	h.c.p.	3.585	5.664	1.773	8.332
Dy	h.c.p.	3.578	5.648	1.769	8.562
Ho	h.c.p.	3.557	5.620	1.759	8.764
Er	h.c.p.	3.532	5.589	1.748	9.164
Tm	h.c.p.	3.523	5.564	1.742	9.346
Yb	c.c.p.	5.468		1.933	7.010
Lu	h.c.p.	3.509	5.559	1.737	9.740
Y	h.c.p.	3.663	5.814	1.814	4.34

¹ α -Pr and α -Nd are distorted somewhat from true h.c.p.

459 (1935); **201**, 656 (1935)] and that the sample has been found to be strongly *ferromagnetic* [Urbain, Weiss, and Trombe, *Compt. rend.*, **200**, 2132 (1935)]. The specific magnetization in an infinite field at absolute zero, $T = 0^\circ \text{K}$, is $\sigma = 253.5 \text{ emu/g}$; the corresponding values of σ for

iron, nickel, and cobalt are 221.8, 57.6, and 163.9 emu/g respectively. The temperature above which metallic gadolinium is paramagnetic rather than ferromagnetic is about 16° C. At low temperatures and in high fields metallic gadolinium is more ferromagnetic than iron.

In spite of the difficulty of preparation, the crystal structures and consequently the densities of the metals are well known. This is so because mixtures of the pure metal and potassium chloride are relatively easily prepared by the reduction of the rare-earth chloride with

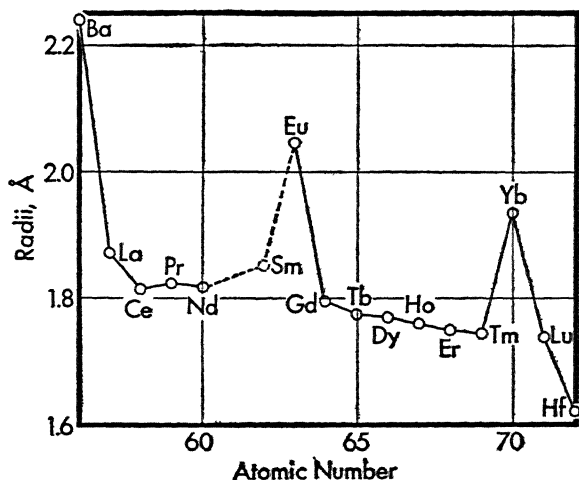


FIG. 8. Atomic radii of the rare-earth elements when the bulk substances are in metallic form.

potassium. The mixture is excellent for X-ray powder photographs, the known spectra of potassium chloride providing a handy calibration. The results are summarized by Bommer [*Z. anorg. allgem. Chem.*, **242**, 277 (1939)], whose results are shown in Table 20. The density of samarium was determined in the mixture by a pycnometric method. There is a striking increase in the atomic radii of europium, ytterbium, and to some extent samarium. They tend to have the radii expected for bivalent metals. This may be seen in Fig. 8, from Klemm and Bommer [*Z. anorg. allgem. Chem.*, **231**, 138 (1937)]. The decrease in radii with increasing atomic number is seen in the other elements. This is the "lanthanide contraction" due to the increased nuclear charge.

Both groups of rare-earth metals are difficult to prepare because of their highly electropositive character. Electrode potentials of these metals have not been accurately measured, and only very approximate

values, indirectly obtained, are known. These are given in Table 21. It will be seen that the rare-earth metals are about as electropositive as metallic magnesium.

TABLE 21
ELECTRODE POTENTIALS OF THE RARE EARTHS¹

	E° , volts
$\text{La}(s) = \text{La}^{+++} + 3e^-$	+2.4
$\text{Ce}(s) = \text{Ce}^{+++} + 3e^-$	2.3
$\text{Pr}(s) = \text{Pr}^{+++} + 3e^-$	2.2
$\text{Nd}(s) = \text{Nd}^{+++} + 3e^-$	2.2
$\text{Sm}(s) = \text{Sm}^{+++} + 3e^-$	2.2
$\text{Eu}(s) = \text{Eu}^{+++} + 3e^-$	2.2
$\text{Gd}(s) = \text{Gd}^{+++} + 3e^-$	2.2
$\text{Tb}(s) = \text{Tb}^{+++} + 3e^-$	2.2
$\text{Dy}(s) = \text{Dy}^{+++} + 3e^-$	2.2
$\text{Ho}(s) = \text{Ho}^{+++} + 3e^-$	2.1
$\text{Er}(s) = \text{Er}^{+++} + 3e^-$	2.1
$\text{Tm}(s) = \text{Tm}^{+++} + 3e^-$	2.1
$\text{Yb}(s) = \text{Yb}^{+++} + 3e^-$	2.1
$\text{Lu}(s) = \text{Lu}^{+++} + 3e^-$	2.1

¹ These rough values were taken mainly from the papers of Noddack and Brukl, *Angew. Chem.*, **50**, 362 (1937); Klemm, *Angew. Chem.*, **51**, 575 (1938); and Kapustinskii, *J. Gen. Chem. U.S.S.R.*, **12**, 193 (1942). The potentials are referred to the standard hydrogen electrode at room temperature.

The metals have metallic luster and appear to be white, gray, or slightly yellow, in general. In order of increasing hardness they are cerium, lanthanum, neodymium, praseodymium, and samarium. Cerium has about the hardness of tin and can be cut with a knife; samarium is about as hard as iron. Their approximate melting points are given in Table 22.

The cerium metals tarnish easily in moist air and ignite at 200–400° C to form the oxides, the heats of formation of the oxides being about the same as those of aluminum oxide and magnesium oxide. Consequently, the metals are strong reducing agents; they liberate hydrogen from cold water slowly and from warm water rapidly. They dissolve easily in dilute acids.

Until recently it was thought that these metals united directly with hydrogen to produce hydrides with the formula RH_3 . There is a great deal of evidence [Emeléus and Anderson, *Modern Aspects of Inorganic Chemistry*, p. 259, D. Van Nostrand Co., New York, 1939] which demonstrates that these "hydrides" are really interstitial compounds in which the hydrogen, in the form of atoms or ions, is accommodated in the interstices between the metal atoms in the crystal lattice. This absorp-

tion of hydrogen occurs slowly at room temperature, and takes place rapidly at 300° C; the resulting compounds are brittle, amorphous solids which are stable in dry air but ignite in the presence of water.

TABLE 22

MELTING POINTS IN °C OF RARE-EARTH METALS AND TRIHALIDES

Rare Earth	Metal, m.p.	Chloride, m.p.	Bromide, m.p.	Iodide, m.p.
La	820-850	850	783	761
Ce	770-800	790-810	732	752
Pr	940-960	769-782	693	733
Nd	800-900	760	684	775
Sm	1350	678	664	816-824
Eu	1100-1200	623
Gd		609	765	926
Tb		588
Dy		654	881	955
Ho		718	914	1010
Er	1250(?)	774	950	1020
Tm		821	...	1015
Yb	About 1800	854	940
Lu		892	...	1045

The hydrogen can be completely removed by heating to 1000° C in a vacuum.

The heats of formation of these interstitial compounds are about the same as for saltlike hydrides, such as LiH and CaH₂. It has been shown that the saltlike hydrides are always denser than the metals from which they are produced, but for the cerium-group interstitial hydrides the metals are denser. It would appear that these interstitial compounds are intermediate in bond type between the definite compounds formed by the alkali metals and those "loosely bound" surface compounds in which hydrogen may be absorbed in varying amounts. Nitrides of the type RN are formed by direct union of the metal with nitrogen at elevated temperatures (about 1000°); their properties are not known. Sulfur combines directly at its boiling point with the metals, producing sulfides of the type R₂S₃, and the halogens combine directly to form the trihalides. Likewise, carbides with the formula RC₂, silicides, phosphides, arsenides, antimonides, and bismuthides are all formed by direct union. Because of the difficulty of obtaining the metals, other methods for the preparation of the above compounds are generally used wherever possible.

Since the anhydrous trihalides are often used for the preparation of the metals and other rare-earth compounds, it is of interest to consider their properties and the methods which are commonly employed for

preparing them. The anhydrous chlorides are often prepared by dehydration of the hydrated chlorides, obtained by treatment of the carbonates or oxides with hydrochloric acid, in an atmosphere of dry hydrogen chloride. They may also be obtained by heating the oxides in sulfur monochloride vapor or in a mixture of sulfur dichloride and chlorine in carbon tetrachloride, by the action of hydrogen chloride on the rare-earth benzoates in ether, and by the reaction of chlorine with the carbides. The tribromides may be prepared similarly. The anhydrous triiodides of La, Ce, Pr, Nd, Sm, and Yb have been prepared by heating the finely powdered oxide with an excess of ammonium iodide at 400°C , and by heating the anhydrous trichlorides just below their melting points with dry hydrogen iodide. By treating hot solutions of the trichlorides with concentrated hydrofluoric acid and washing the precipitated fluoride repeatedly with absolute alcohol, the anhydrous fluorides may be obtained. They may also be prepared by the action of fluorine on the carbides.

In Table 22 are tabulated the approximate melting points of the trihalides.* They are hygroscopic solids and, with the exception of the fluorides, are readily soluble in water. The iodides are yellowish to dark green powders, very soluble in pyridine and alcohol, and they change in moist air to basic iodides. It has been shown that the halides distribute themselves between water and alcohols, ketones and ethers, and this property has been used to separate some of the rare earths in analytical procedures [Fischer, Dietz, and Jübermann, *Naturwissenschaften*, **25**, 348 (1937)]. The chlorides easily absorb ammonia, forming series of ammoniates with 2, 4, 8, 12, and 20 molecules of ammonia per molecule of trichloride; the dissociation pressures have been measured for the cerium ammoniates. Oxychlorides are formed without difficulty when the hydrated chlorides are heated in air; they are insoluble in water.

Chlorates of the yttrium metals have been prepared by the addition of barium chlorate to solutions of the rare-earth sulfates. Bromates and iodates have been prepared in a similar way [see the papers of Zernicke and James, *J. Am. Chem. Soc.*, **48**, 2871 (1926), and of Harris, *J. Am. Chem. Soc.*, **53**, 2475 (1931)], and they have been used extensively in certain rare-earth separations.

A sesquioxide, R_2O_3 , is formed by each of the rare-earth elements, and the term "rare earths" originally meant the sesquioxides. All these oxides are stable toward oxidation in air at room temperature, and only with cerium, praseodymium, and terbium is there any oxida-

* Taken chiefly from the paper of Jantsch and Wein, *Monatsh.*, **69**, 161 (1936). The melting points of the fluorides do not appear in the literature.

tion to higher oxides even at a bright red heat.* With the exception of these three elements, the sesquioxides are easily prepared by ignition of the hydroxides, carbonates, oxalates, sulfates, nitrates, and the salts of many other oxyacids, as well as by the direct combustion of the free metals. The sesquioxides of praseodymium and terbium may be obtained from the higher oxides, ordinarily produced by the above methods, by reduction in a stream of hydrogen at 900°. The reduction of ceric oxide to the sesquioxide by means of hydrogen is much more difficult because of the great stability of the higher oxide, and the reduction is found to be reasonably rapid only at very high temperatures (about 2000°) in hydrogen at a pressure of 150 atm. Cerium sesquioxide has also been prepared by reduction of cerium dioxide with calcium, followed by washing out the other reaction products with a solution of ammonium chloride at -10° C.

All the sesquioxides are soluble in acids, but the rate of solution is greatly dependent on the method of preparation of the oxide and in particular on the temperature of ignition or calcination. They readily form normal salts with even such weak acids as carbonic, chromic, formic, and acetic acids, being fairly strong basic anhydrides (stronger than MgO but weaker than the alkaline earths). For example, pure neodymium is pale blue; on standing in moist air it turns pink owing to absorption of carbon dioxide and water. The hydrous oxides, or hydroxides, produced (usually in a gelatinous condition) when an excess of ammonium or alkali hydroxide is added to a warm solution of a soluble rare-earth salt, are all comparatively insoluble in water. For this reason the hydroxides do not give rise to very high concentrations of hydroxyl ion, even though the metals are fairly reactive.†

The basicities‡ differ considerably, however, among the various members of the group. By taking the basicity of dysprosium hydroxide as unity, the relative basicities are about as follows: La 2500, Pr 150, Nd 100, Sm 20, Gd 7, and Dy 1. It has been found that lanthanum is by far the most basic of the entire rare-earth group, and it is very

* When cerium sesquioxide is exposed to air at room temperature there is a very slow conversion to the dioxide.

† The solubility products $(R^{+++})(OH^{-})^3$ have been estimated to be about 10^{-19} for lanthanum, 10^{-20} for cerium and praseodymium, 10^{-22} for gadolinium, and 10^{-24} for lutecium.

‡ The term basicity has not been defined precisely, and the sense of the word varies with the user. One easily understood usage is that basicity is the strength of the hydroxides as bases; the extent of hydrolysis of aqueous solutions of soluble rare-earth salts of strong acids would provide a similar measure of basicity. Not infrequently, chemical intuition born of experience provides an investigator with a feeling for the meaning of *basicity*.

likely that lanthanum hydroxide is the strongest trivalent base known. This activity is so great that lanthanum sesquioxide hisses in moist air much like quicklime. The relative basicities have been determined in a number of different ways, and the results have been excellently summarized by Moeller and Kremers [*Chem. Rev.*, **37**, 97 (1945)]. It has been established that the order of decreasing basicity throughout the rare-earth group is the same as the order of increasing atomic number.* These differences in basicity are of much value in the problem of the separation of rare earths. For example, the concentration of element 61 by methods of fractional crystallization is practically impossible because this element is expected to be always associated with other rare earths whose salts are nearly equal in solubility.

By applying the method of intensifying the differences in basicity, it has been claimed that 15 basicity fractionations are about as effective as 1000 fractionations of the double magnesium nitrates in the concentration of element 61; and it may be that this method may eventually be successful in isolating a weighable amount of this elusive element should it actually exist in nature and have the predicted properties.

The relatively high basicities of the rare earths are evident from the ready formation of their carbonates. The hydroxides absorb carbon dioxide readily from the air, forming granular carbonates. Crystalline carbonates are obtained by passing carbon dioxide into a suspension of the hydroxides and by adding an alkali carbonate to a neutral rare-earth solution. The solubility of the carbonates in ammonium carbonate increases with the atomic number. Both the sodium and ammonium double carbonates are less soluble than the corresponding potassium compounds, and this fact is often utilized in fractionations.

The sulfates of the rare earths are made by dissolving the hydroxides, carbonates, or oxides in dilute sulfuric acid. They form with varying amounts of water of crystallization, and their solubility in water decreases with increasing temperature. Many rare-earth atomic weights have been determined by means of the sulfates. When an excess of acid is used, hydrosulfates are formed which in turn decompose into the normal salts when heated. If the normal salts are heated, oxysulfates of the type $R_2O_2SO_4$ are formed. Sulfides, sulfites, thiosulfates, dithionates, thiocyanates, selenates, and selenites of the rare earths have also been made.

Nitrates of the cerium group, $R(NO_3)_3 \cdot 6H_2O$, are crystalline, whereas those of the yttrium group do not crystallize easily; all are deliquescent,

* The basicity of yttrium (No. 39) is intermediate between that of dysprosium (No. 66) and that of holmium (No. 67), and scandium, thorium, and tetravalent cerium follow lutecium in that order.

soluble in water and alcohol, but not very soluble in nitric acid. They are obtained by treatment of the oxides, carbonates, or hydroxides with nitric acid. When the nitrates are heated, basic nitrates are formed which are insoluble in water. Double nitrates of the cerium group elements are easily formed and are useful in separating members of this group.

The phosphates are found in nature. They are easily precipitated in a gelatinous form by the addition of a solution of alkaline phosphates or phosphoric acid to a solution of rare-earth salts. Hypophosphites, pyrophosphates, and various complex phosphates are also known.

Since the rare-earth oxalates are insoluble in acids they are of great use. The addition of oxalic acid to a solution containing rare-earth salts and free mineral acid precipitates the rare earths as oxalates, and this makes possible a separation from the common metals. However, reprecipitation is always necessary as the oxalates occlude many other salts. The solubilities of the decahydrated oxalates in water are all about 1×10^{-6} mole per liter.

Numerous other compounds are known, among which are molybdates, chromates, uranates, columbates, tantalates, tungstates, formates, acetates, tartrates, benzoates, citrates, and succinates.

Some of the solubility properties of a number of the more important rare-earth trivalent compounds are summarized in Table 23.

TABLE 23

SOLUBILITY PROPERTIES OF SOME RARE-EARTH TRIVALENT COMPOUNDS

	Cerium Group (57 to 62)	Yttrium Group (63 to 71)
Carbonates	Insoluble in water and in $(\text{NH}_4)_2\text{CO}_3$ solution.	Insoluble in water; soluble in $(\text{NH}_4)_2\text{CO}_3$ solution.
Hydroxides	Somewhat soluble in water	Slightly soluble in water.
Fluorides	Insoluble in water.	Insoluble in water.
Formates	Slightly soluble in water.	Moderately soluble in water.
Nitrates	Soluble in water; less soluble in HNO_3 usually.	Soluble in water; less soluble in HNO_3 ($\text{Gd}(\text{NO}_3)_3$ especially).
Basic nitrates	Moderately soluble in water.	Slightly soluble in water.
Double nitrates (e.g., Mg_2R $(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$)	Easily crystallized.	Not easily crystallized.
Oxalates	Very insoluble in water and in $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution.	Very insoluble in water; soluble in $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution.
Phosphates	Insoluble in water.	Insoluble in water.
Potassium sulfates $(\text{K}_2\text{R}(\text{SO}_4)_2)$	Insoluble in K_2SO_4 solution.	Soluble in K_2SO_4 solution.

Evidence for the existence of compounds in which the rare earth has a valence other than 3 has already been presented. Such compounds are interesting not only because of the information they give on the electronic configurations and the relations of one rare earth to another but also because they offer an attractive approach to the problems of separating and determining the various members of the group.

More is probably known about tetrapositive cerium than any of the other non-tripositive states of rare earths. Ceric oxide, CeO_2 , is easily obtained as an amorphous powder when cerous or ceric hydroxide, nitrate, sulfate, or salt of a volatile oxyacid is heated in air, the oxalate being most used for this purpose. The oxide is white when pure but is often colored light yellow to dark orange, especially when heated, seemingly because of traces of praseodymium or possibly because of colored polymorphic forms. Crystalline ceric oxide is remarkably resistant to attempts to dissolve it with hydrochloric or nitric acids or with alkali hydroxides; in fact, fused sodium hydroxide has no measurable action on it. However, if reducing agents, such as hydrogen peroxide or stannous chloride, are used in addition, solution is effected with the production of a cerous salt.

The hydrous ceric oxides are dissolved much more readily. Warm concentrated sulfuric acid * converts ceric oxide into yellow ceric sulfate quantitatively, and this is the usual method of preparing a solution of a ceric salt; dilute sulfuric acid has no perceptible action on the oxide. Other salts are easily prepared by displacement, by the action of acids on the hydroxide, by anodic oxidation of the corresponding cerous salt [see the paper of Neckers and Kremers, *J. Am. Chem. Soc.*, **50**, 955 (1928), for a description of the anodic oxidation process], or by oxidation with peroxysulfate, lead dioxide, sodium bismuthate, and nitric acid.

When ammonia or an alkali hydroxide is added to a solution of any ceric salt, a yellow gelatinous ceric hydroxide is produced which is insoluble in an excess of alkali. When the precipitate is treated with concentrated hydrochloric acid, chlorine is evolved and cerous chloride is produced. Ceric chloride is known only in solution and is unstable. Ceric hydroxide is a weak base, and solutions of the salts are therefore hydrolyzed to some extent. Reduction of ceric salts to cerous salts is effected easily in acid solutions by such reducing agents as hydrogen peroxide, nitrous acid, sulfurous acid, hydriodic acid, and alcohol. Ammonium nitrate in concentrated nitric acid solution gives with ceric salts a relatively insoluble compound, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, which can be

* If the concentrated sulfuric acid is boiling, oxygen is given off and cerous sulfate is formed.

used to obtain cerium in a pure form. Hydrated ceric hydrophosphate, $\text{Ce}_2\text{H}(\text{PO}_4)_3 \cdot 12\frac{1}{2}\text{H}_2\text{O}$, is obtained as a yellow precipitate when sodium phosphate is added to an acid solution of a ceric salt; cerium can therefore be separated from other rare earths by this means, since the phosphates of the tripositive earths are moderately soluble in acids.

The oxidation-reduction potentials of cerous-ceric salts have been investigated by a number of workers. The formal potential * in sulfuric acid solution has been found to be -1.461 volts in $0.5 f \text{ H}_2\text{SO}_4$ and -1.443 volts in $1.0 f \text{ H}_2\text{SO}_4$ at 25°C [Kunz, *J. Am. Chem. Soc.*, **53**, 98 (1931); see also Baur and Glaessner, *Z. Elektrochem.*, **9**, 534 (1903)]. These values, considered with the potentials in other solutions, indicate that there is considerable complex-ion formation between the ceric ions and the sulfate (or hydrosulfate) ions. In nitric acid solutions of the nitrates the formal potential is nearly independent of nitric acid concentration between $0.5 f$ and $2 f$ nitric acid, having the value -1.61 volts at 25°C [Noyes and Garner, *J. Am. Chem. Soc.*, **58**, 1265 (1936)]. This constancy of the potential was originally thought to indicate that there was no appreciable complex-ion formation between the ceric ions and nitrate ions, but in view of more recent knowledge it seems that some $\text{Ce}(\text{NO}_3)_6^{--}$ ions may be produced. The results could then be explained by assuming some nitrate complex-ion formation with the cerous ions, or that hydroxide also participated in the complex-ion formation with the ceric ions.†

Evidence for a nitrate complex of ceric cerium includes the following: excess nitric acid does not salt out a ceric salt from a nitric acid solution of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, but excess ammonium nitrate does; crystalline $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ does not hydrolyze to insoluble ceric salts when dissolved in water, whereas $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_3$, a "double" salt, does; transference experiments in $6 f \text{ HNO}_3$ indicate that cerium is in an anion complex. [Meyer and Jacoby, *Z. anorg. Chem.*, **27**, 359 (1901); Duval, *Bull. soc. chim.*, **5**, 5, 1020 (1938); also unpublished experiments of Garner. Other chemical evidence is presented by Smith, Sullivan, and Frank, *Ind. Eng. Chem., Anal. Ed.*, **8**, 449 (1936).] This nitrate complex of cerium is interesting because only two other examples of nitrate complexes are known, a thorium nitrate complex and a nitrate

* The formal potential differs from the molal potential in that no correction is made for activity coefficients, hydrolysis, complex-ion formation, or ionization in the former, and it is actually of more practical value when dealing with relatively concentrated salt and acid solutions. The potentials are customarily referred to the molal hydrogen electrode.

† Unpublished preliminary transference experiments of C. S. Garner gave no evidence of cerium migration towards the anode in $2 f \text{ HNO}_3$. The $\text{Ce}(\text{NO}_3)_6^{--}$ complex may be largely dissociated in this low nitric acid concentration.

complex of argentic silver, the formulas of which have not been definitely established. Moreover, it accounts for the fact that ceric cerium can be cleanly separated from nitric acid solutions of the other rare earths which do not appear to form such complexes. The nature of the bonding in nitrate complexes would be interesting to study. In 2 *f* HCl the formal potential of cerous-ceric chlorides is -1.28 volts [Smith and Getz, *Ind. Eng. Chem., Anal. Ed.*, 10, 191 (1938)]. The formal potential of cerous-ceric perchlorates in 1 *f* HClO₄ is -1.7 volts at 25° C.,* a value much higher than those obtained in other solutions and one which probably approaches the molal potential more closely.

Ceric perchlorate solutions are somewhat unstable owing to the oxidation of the water by the free ceric ions in the absence of any stabilizing complex-ion-forming substance, and they cannot be prepared by oxidation of cerous perchlorate with hot concentrated perchloric acid. Anodic oxidation is used to obtain such solutions.

The photochemical reduction of ceric ions in perchloric acid by water has been studied [Weiss and Porret, *Nature*, 139, 1019 (1937)]. Pure oxygen is evolved at a measurable rate when a solution 0.1 *f* in Ce(ClO₄)₄ and 1 *f* in HClO₄ is irradiated with filtered ultraviolet light, the rate decreasing in the presence of an increasing concentration of cerous ions. (Perchlorate ions are substantially non-absorbing in the ultraviolet and do not decompose under these conditions.) On irradiating solutions of ceric sulfate in sulfuric and mixed sulfuric-perchloric acids there is no measurable evolution of oxygen, since there are not many free ceric ions.† The quantum yield is low (about 0.1).

If a cerous salt is precipitated with ammonia and an excess of hydrogen peroxide is added, a reddish brown unstable precipitate of perceric hydroxide is formed. It has been shown that its formula is CeO₃·2H₂O.

* Unpublished preliminary experiments of C. Garner. The potential was also determined in much more concentrated HClO₄ by Smith and Getz (*loc. cit.*), who concluded that the complex (Ce(ClO₄)₆)²⁻ is formed under such conditions. Their experiments, however, can be explained in other ways, and it is thought unlikely that such a complex is formed, particularly in the more dilute HClO₄ solutions. The evidence in the following two paragraphs confirms this belief. Quite recently an extensive study of the potential in perchloric acid was made by Sherrill, King, and Spooner [*J. Am. Chem. Soc.*, 65, 170 (1943)]; their value of the formal potential in 1 *f* HClO₄ is -1.7000 volts at 25° C.

† The mechanism proposed by Weiss and Porret is as follows:

- (1) $\text{Ce}^{++++} + h\nu \rightarrow \text{Ce}^{++++*}$
- (2) $\text{Ce}^{++++*} + \text{H}_2\text{O} \rightarrow \text{Ce}^{+++} + \text{H}^+ + \text{OH}^-$
- (3) $2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}, 2\text{O} = \text{O}_2$
- (4) $\text{Ce}^{+++} + \text{OH}^- \rightarrow \text{Ce}^{++++} + \text{OH}^-$

This is not evidence for a hexavalence of cerium, however, since experiments have shown that the cerium is tetravalent. This behavior of cerium sometimes serves as a test for traces of this element. When an excess of warm, concentrated potassium carbonate solution is added to a rare-earth solution until the initial precipitate redissolves, the solution will become yellow on the addition of hydrogen peroxide if a trace of cerium is present. If the cerium is present in large amounts, the addition of hydrogen peroxide turns the solution a dark red color owing to the formation of potassium perceric carbonate; the addition of still more hydrogen peroxide lightens the color and eventually precipitates the cerium in an unknown state.

Because of the high oxidation potential of ceric salts and the stability of their solutions in general they are employed in analytical chemistry. A number of visual indicators have been developed for use with ceric sulfate solutions.*

Samarous compounds in which the samarium is clearly divalent are now well known. In general, three methods are available for the production of divalent compounds of the rare earths: (1) reduction of the anhydrous trihalides with hydrogen, ammonia, or aluminum at high temperatures; (2) thermal decomposition of the triiodides; and (3) electrolytic reduction of the trivalent ion in the presence of sulfate ion, with the consequent precipitation of the insoluble sulfate. Electrolytic reduction cannot be used in aqueous solutions because divalent samarium reacts rapidly with water according to the equations:



Attempts to so prepare samarous compounds with a mercury cathode and high current densities were unsuccessful [Pearce, *Chem. Revs.*, **16**, 121 (1935)]. However, the first method mentioned has been widely used. [This method of reduction was discovered by Matignon and Cazes (*loc. cit.*); see also *Compt. rend.*, **142**, 83, 276 (1906).] The samarium trichloride is completely dehydrated in a current of hydrogen chloride, the temperature being held two hours at 90° C, an hour at 130° C, and then raised to 250° C for a few minutes. Pure dry hydrogen at atmospheric pressure is then used to displace the hydrogen

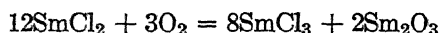
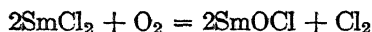
* For discussions of analytical applications of ceric sulfate solutions see the papers of Willard and Young, *J. Am. Chem. Soc.*, **50**, 1322, 1334, 1368, 1376, 1379 (1928); **51**, 139, 149 (1929); **52**, 36, 132, 553, 557 (1930); Furman *et al.*, *J. Am. Chem. Soc.*, **50**, 755, 1675 (1928); **51**, 1128, 1449 (1929); **52**, 1443, 2347 (1930); **53**, 1283, 2561 (1931).

chloride, after which the temperature is slowly raised to 740° (m.p. of the dichloride) and held there for five hours, the hydrogen stream being continued. The reaction is $2\text{SmCl}_3 + \text{H}_2 = 2\text{SmCl}_2 + 2\text{HCl}$. The progress of the reduction is observable by noting the deepening of the color, samarium dichloride having a deep red-brown color. The reaction is complete when hydrogen chloride is no longer evolved. The yield is from 50 to 90% pure samarium dichloride, the remainder being samarium trichloride. The dibromide, which is darker colored than the dichloride, has been prepared similarly [Prandtl and Kögl, *Z. anorg. allgem. Chem.*, **172**, 265 (1928)]; it melts at about 700° . The dichloride has also been prepared by reduction with ammonia in a like manner [Jantsch, Rüping, and Kunze, *Z. anorg. allgem. Chem.*, **161**, 210 (1927)], the reaction, which is slow and reversible, being:



When porcelain boats were used to contain the salt during the reduction, silicon was formed, presumably as the result of the partial decomposition of the dichloride into the trichloride and metallic samarium. The nearly black diiodide has been prepared by the thermal decomposition of samarium triiodide in a high vacuum at $800\text{--}900^{\circ}$ [Jantsch and Skalla, *Z. anorg. allgem. Chem.*, **193**, 391 (1930); they also prepared the dibromide by thermal decomposition of the tribromide]. Jantsch and Skalla prepared samarous sulfate, chromate, and phosphate by double decomposition reactions with the dichloride.

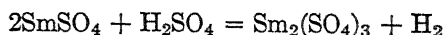
The samarous chloride is soluble in water but extremely unstable even if oxygen is excluded. In air it reacts according to the equations:



It is insoluble in liquid ammonia, sulfur dioxide, hydrogen cyanide, phosphorus trichloride, phosphoryl chloride, sulfuryl chloride, stannic chloride, benzene, toluene, chloroform, pyridine, alcohols, ketones, and esters, but slightly soluble in molten sodium chloride. If heated much above its melting point, it slowly decomposes into samarium and the trichloride. The dibromide has similar properties. The diiodide gives a deep Bordeaux-red solution when it is dissolved in water; the color slowly disappears and hydrogen is evolved as it decomposes. On heating the solid diiodide to 560° decomposition begins moderately rapidly according to the reaction:



The chromate, sulfate, and phosphate are all insoluble in water, the sulfate being a bright orange salt, soluble with decomposition in dilute acids:



The formal reduction potential of samarous-samaric salts has been estimated to be about +0.8 volt [Latimer, *Oxidation Potentials*].

Europous chloride, EuCl_2 , was first prepared in 1911 by the high-temperature reduction of anhydrous europic chloride by hydrogen at 450°C [Bourion and Urbain, *Compt. rend.*, **153**, 1155 (1911)]. This method has also been used to prepare the diiodide and the yellow difluoride [Jantsch, Alber, and Grubitsch, *Monatsh.*, **53-54**, 305 (1929); Beck and Nowacki, *Naturwissenschaften*, **26**, 495 (1938)]. However, the diiodide is best prepared by heating the hydrated triiodide with ammonium iodide in a stream of hydrogen iodide and hydrogen. Pure brown-violet europous sulfide, EuS , has also been prepared by heating europic sulfate in a current of hydrogen sulfide (Beck and Nowacki, *loc. cit.*). The europous sulfide so prepared is insoluble in water but easily soluble in dilute acids.

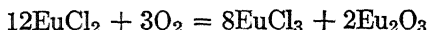
Attempts have been made to reduce europic oxychloride, EuOCl , with hydrogen at high temperatures but without success. Electrolytic reduction of a solution of the trichloride at a mercury surface was found by Yntema to give dipositive europium [Yntema, *J. Am. Chem. Soc.*, **52**, 2782 (1930)]. A two-compartment cell was used which required 65 volts to give a current of 0.18 ampere. Sulfate ion was present, and colorless, insoluble europous sulfate, EuSO_4 , formed which could be filtered out, giving a good separation of europium from most of the other rare earths. It has been found [McCoy, *J. Am. Chem. Soc.*, **58**, 1577 (1936)] that the electrolysis of the formate (made from europium sesquioxide and formic acid) can be carried out more simply. A one-compartment cell can be used with a mercury cathode at the bottom and a platinum wire anode enclosed in an upturned glass tube below the surface of the solution. With 50 ml of 0.1 *f* europic formate, 6 volts give a current of about 0.1 ampere, carbon dioxide and hydrogen forming at the anode, and europous ion at the cathode. When about 80% of the europic formate has been reduced, hydrogen starts to be liberated at the cathode and the current efficiency becomes smaller. Sulfate ion can be added if desired, and europous sulfate precipitated. The acetate may be similarly electrolyzed.

If a silver anode is used, a chloride solution can likewise be electrolyzed, either with a mercury or platinum cathode. The divalent chloride has also been obtained (W. Pearce, master's thesis, University of

Illinois, 1931) by sifting into the aqueous trichloride solution (to which a small amount of sulfuric acid was added) powdered magnesium, aluminum, or iron; reduction with stannous chloride, ferrous sulfate, hypophosphorous acid, hydroxylamine sulfate, and hydrazine sulfate was unsuccessful. Reduction with zinc in a Jones reductor may be convenient for preparing dipositive europium.

The formal reduction potential of europous-europic salts has been studied by McCoy (*loc. cit.*) and its value is +0.43 volt at 25° C, in good accord with the powerful reducing properties of europous compounds.

Europous compounds are, in general, much more stable than samarous compounds. White europous chloride dissolves in water, giving a fairly stable, nearly colorless solution if air is excluded.* In air the more or less rapid reaction



takes place.† Hydrogen is evolved from its aqueous solutions, slowly at room temperature and more rapidly at higher temperatures.



The diiodide is a very dark, brownish green, but its aqueous solution is nearly colorless and decomposes slowly at room temperature with the evolution of hydrogen. The difluoride is so rapidly oxidized by air that a filter paper containing it is set on fire. White, crystalline europous sulfate is rather stable in air,‡ and two crystalline habits are known: the α form occurs as feathery needles and is usually formed when europous chloride from a Jones reductor is run into dilute sulfuric acid; the β form is more compact and granular and is more stable. The α form is dissolved by 3N H_2SO_4 , whereas the β form is but slightly soluble. Europous sulfate is oxidized readily by chlorine, bromine, nitric acid, and many other oxidizing agents. If the sulfate is boiled for a short time with a solution 1 normal in sodium carbonate and 0.4 normal in sodium hydroxide, a light yellow, easily filtered carbonate (probably EuCO_3) is formed, which dissolves in most acids, and

* A 30% solution of EuCl_2 has a greenish yellow color, the absorption spectrum of which shows nearly complete absorption of visible light below about 4480 Å.

† McCoy (*loc. cit.*) who has studied the rate of oxidation of EuCl_2 solution by air, found that a 0.05 *f* solution was half oxidized in about five minutes if a rapid stream of air was blown through it.

‡ A sample corked up in a vial was found to have been only 2.8% oxidized at the end of 143 days. Its resistance to oxidation is probably chiefly due to its insolubility.

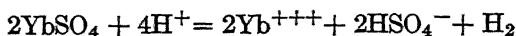
which is therefore convenient for the preparation of a number of divalent salts. If europous carbonate is dissolved in perchloric acid, black europous perchlorate, $\text{Eu}(\text{ClO}_4)_2$, is formed which is moderately insoluble in water.

Europium is usually isolated and purified by the europous sulfate method [McCoy, *J. Am. Chem. Soc.*, **57**, 1756 (1935); Yntema, *J. Am. Chem. Soc.*, **52**, 2782 (1930); Selwood, *J. Am. Chem. Soc.*, **57**, 1145 (1935)]. If a mixture of earths is too dilute in europium to give a precipitate of europous sulfate, dilute barium chloride solution is added to the electrolytic bath and the barium sulfate which is formed nearly completely coprecipitates all the europous ion present. The europium is then recovered from the barium sulfate by repeated washing with hot concentrated nitric acid. Ytterbium, if present, will also be removed with the europium. Europous compounds may be titrated with permanganate or iodine solutions provided that other reducing agents, including ytterbous salts, are not present. It is often better to add excess ferric sulfate before proceeding with the titration with permanganate [McCoy, *J. Am. Chem. Soc.*, **61**, 2455 (1939)].

It is of interest to mention that perchlorate ion is not reduced in dilute solutions by europous compounds at room temperature but hydrogen is slowly formed (R. A. Cooley, unpublished experiments).

What has been said about the preparation and properties of europous compounds is also largely true of the ytterbous compounds.

Ytterbium dichloride was first prepared in 1929 by the hydrogen reduction of anhydrous ytterbium trichloride [Klemm and Schüth, *Z. anorg. allgem. Chem.*, **184**, 352 (1929)]. The reduction took place over a period of six hours at 620°C . Thermal decomposition of the trihalides in a vacuum resulted in the production of ytterbium diiodide (black by reflected light, red by transmitted light), dibromide (golden-yellow), and dichloride (light gray, nearly white) [Jantsch, Skalla, and Jawurek, *Z. anorg. allgem. Chem.*, **172**, 207 (1931)]. Halogen was split off at about 250° for the triiodide, 700° for the tribromide, and about 870° for the trichloride. The electrolytic reduction of ytterbic compounds [Yntema, *J. Am. Chem. Soc.*, **52**, 2782 (1930); Ball and Yntema, *J. Am. Chem. Soc.*, **52**, 4264 (1930); Pearce, Naeser and Hopkins, *Trans. Electrochem. Soc.*, **69**, 557 (1936); Marsh, *J. Chem. Soc.*, **1937**, 1367] in dilute sulfuric acid gives yellow-green ytterbous sulfate, YbSO_4 . As soon as electrolysis is stopped, the ytterbous sulfate reacts rapidly with the sulfuric acid present:



Although the reaction would be slower in a lower hydrogen-ion concentration, it has been found that the optimum conditions for the precipitation of ytterbous sulfate are obtained when solutions 0.6 *f* in sulfuric acid and 0.4 *f* in ytterbic sulfate are electrolyzed at a current density of about 0.1 ampere per square centimeter. Under these conditions the precipitate is granular rather than feathery, the granular form being less soluble in acid. About 10% of the ytterbium is left in solution owing to the incomplete reduction, the slight solubility of ytterbous sulfate, and the reaction with the acid before the precipitate can be effectively filtered and washed. Ytterbium oxide of 99.9% purity has been prepared from the sulfate obtained in this way.

The dichloride dissolves in water, giving a yellow-green solution which slowly evolves hydrogen. When the solid is heated near the melting point, it decomposes into the trichloride and metallic ytterbium. The behavior of the other dihalides is similar. The selenide and telluride of dipositive ytterbium have also been prepared [Senff and Klemm, *Z. anorg. allgem. Chem.*, **242**, 92 (1939)].

The ytterbous-ytterbic couple was found by Walters and Pearce [*J. Am. Chem. Soc.*, **62**, 3330 (1940)] to have the value +0.578 volt at 23° in 1 *f* acetic acid solution. This value is in agreement with the value +0.6 volt estimated by Latimer [*Oxidation Potentials*]. Laitinen, however, has pointed out that tripositive ytterbium is not reduced by zinc although this would be expected from a potential of 0.6 volt; he found the value +1.15 volts from the dropping mercury electrode [*J. Am. Chem. Soc.*, **64**, 1133 (1942)]. This value seems more nearly correct, and it is probable that the platinum electrode used by Walters and Pearce was functioning partly as a hydrogen electrode.

A summary of the formal reduction potentials mentioned in this section is given in Table 24.

TABLE 24
FORMAL REDUCTION POTENTIALS (25° C)

Half-Reaction	E_0' , volts	
$\text{Ce}^{+++} = \text{Ce}^{++++} + e^-$	-1.28(2 <i>f</i> HCl)	-1.44(1 <i>f</i> H ₂ SO ₄)
	-1.61(1 <i>f</i> HNO ₃)	-1.70(1 <i>f</i> HClO ₄)
$\text{Pr}^{+++} = \text{Pr}^{++++} + e^-$	-1.6 (estimated)	
$\text{Sm}^{++} = \text{Sm}^{+++} + e^-$	About +0.8 (estimated)	
$\text{Eu}^{++} = \text{Eu}^{+++} + e^-$	+0.43 (very dilute HCOOH)	
$\text{Yb}^{++} = \text{Yb}^{+++} + e^-$	+1.15	

It is not unduly optimistic to think that many of the other rare earths may eventually be obtained in these interesting valence states.

As the tedious work of separating the members of this group of elements is facilitated by the use of these non-tripositive states of the rare earths, a sphere of research which has been relatively little investigated may thus be made available for many to study. Indeed, it is to be hoped that the reactions of these non-tripositive compounds will be studied much more extensively in the future.

Appendix 1

NUCLEAR PROPERTIES OF THE RARE-EARTH ELEMENTS

Because some of the rare earths appear directly or indirectly as fission products when uranium and thorium are bombarded with neutrons, and because the nuclear properties of some of these elements are noteworthy, it is of interest to include here the currently available information on the nuclear properties of the rare-earth elements. In general, nuclear studies of these elements have not been extensive as there are many difficulties associated with the separation of the members of this group and consequent uncertainties in the purity of the materials available for investigation.

The most recent and comprehensive published table of radioactive and stable isotopes and literature references is due to G. T. Seaborg [*Rev. Mod. Phys.*, **16**, 1 (1944)]. Several more recent data have been published by workers on the Manhattan project [*Science*, **103**, 697 (1946)]. We shall, in Table I, present the data for the rare-earth elements, following the nomenclature adopted by Seaborg.

The extent of certainty of the assignment of each radioisotope is given in the column headed "class" by a letter according to the following notation:

- A = isotope certain (mass number and element certain).
- B = isotope probable, element certain.
- C = one of few isotopes, element certain.
- D = element certain.
- E = element probable.
- F = insufficient evidence.
- G = probably in error (e.g., impurity or inadequate half-life value).

It may be noted that the majority of the assignments for the rare earth fall in classes D, E, F, and G.

The types of radiation observed for each radioisotope are indicated in the table under the heading "radiation," with the following symbols:

- β^- = negative beta-particles.
- β^+ = positive beta-particles (positrons).
- γ = gamma-rays.

- α = alpha-particles.
 e^- = internal-conversion electrons.
 K = orbital electron capture.
 IT = isomeric transition (transition from upper to lower isomeric state).

Annihilation gamma-rays are not listed. All energies in the table are expressed in millions of electron volts, Mev. It should be pointed out that the gamma radiation emitted by a radioisotope consists ordinarily

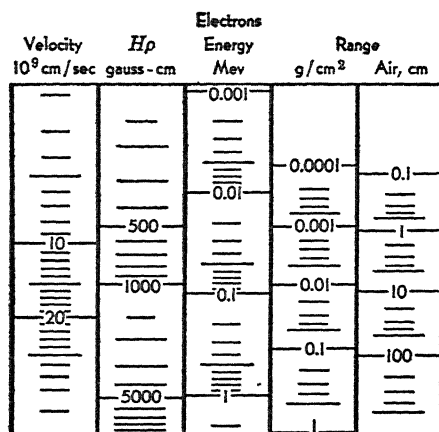


FIG. 1. Nomograph relating velocity, radius (ρ) of the circular orbit in a magnetic field of intensity H , range in arbitrary substances and in air, and energy, for monoenergetic electrons.

of one or more nearly monochromatic spectral lines of the energy or energies shown. Beta radiation from a radioactive substance, on the other hand, consists of negative electrons (or positrons) whose energies are spread continuously over the range from zero to a characteristic maximum value. It is this maximum energy which is given in the table, but it is important to note that the maximum intensity of the beta radiation observed with a given sample is generally due to the particles of somewhat less than one-half the maximum energy. Figure 1 at the end of the table shows graphically some useful quantitative relations between the energy of moving electrons (homogeneous energy) and their velocity, radius of path ρ in a magnetic field H ($H\rho = mvc/e$), and their range in air and other substances. Alpha-particles emitted by radioactive elements are nearly equal in energy; discrete alpha energy spectra are known, but the number of such groups of alpha-particles for a given isotope is small.

The nuclear reaction producing a given isotope, indicated in the last column of the table, is represented by a now commonly adopted notation. The target element, projectile, and outgoing particle are listed in that order (p = proton, n = neutron, d = deuteron, α = alpha-particle, γ = gamma-ray). For example, $\text{Ce-}n\text{-}p$ represents a nuclear reaction in which cerium is bombarded with neutrons, protons are emitted, and an isotope of lanthanum is formed. The neutron-induced fission reactions of the heavy elements are indicated by the notation $\text{U-}n$ and $\text{Th-}n$. Where it is known that a fission product is other than the first element in a chain decay it is listed as formed by the beta decay of its immediate parent isotope. The most recent openly published statements about the fission process are those of L. A. Turner [*Rev. Modern Phys.*, **17**, 292 (1945)] and Lise Meitner [*Rev. Modern Phys.*, **17**, 287 (1945)]. Other interesting articles on fission and the transuranic elements are in the official Smyth report [*Atomic Energy for Military Purposes*, Princeton University Press, 1945] and in the *Physical Review*: Turner, **69**, 366 (1946); Seaborg, McMillan, Kennedy, and Wahl, 366; Seaborg, Wahl, and Kennedy, 367; Kennedy and Wahl, 367; Kennedy, Seaborg, Segrè, and Wahl, **70**, 555 (1946); and in *Science*, Seaborg, **104**, 379 (1946).

The rare earths are also noteworthy for the fact that they are, as a class, good absorbers of slow neutrons; indeed, gadolinium seems to be the best known absorber of slow neutrons. Quantitatively, the absorptive power of an element may be expressed by the coefficient σ in the expression

$$\frac{I}{I_0} = e^{-N\sigma x}$$

where I_0 and I are the intensities of the incident and emergent beam of neutrons respectively, x is the thickness (in centimeters) of the absorbing element, and N is the number of nuclei per cubic centimeter of the absorber. The dimensions of σ are square centimeters, and it is customary to call σ the absorption cross section for neutrons. The unit used for σ is the "barn," one barn being equal to 10^{-24}cm^2 . Depending upon the way in which the absorption measurements are made, the results may be interpreted in terms of elastic and inelastic scattering of the neutrons, total absorption, and radiative capture of neutrons to produce the isotope of next higher mass number. Neutrons may be removed from the beam by nuclear transmutation of the target nuclei with emission of heavy nuclear particles such as alpha-particles or protons; cross sections for such processes may be determined also.

TABLE I
 RADIOACTIVE AND STABLE ISOTOPES OF THE RARE EARTHS

Atomic Number Z	Isotope	Class	Abundance %	Radiation	Half-Life	Energy of Radiation, Mev		Formed by the Nuclear Reaction
						β	γ	
57	A							
	La^{137}	B		K, γ	17.5 hr		0.88	Ba-d-n Ba-p-n La-n-2n(?)
	La^{138}	F			2.2 hr			
	La^{139}		100		Stable			
	La^{140}	A		β^- , γ	40.0 hr	1.41	1.63	La-d-p La-n- γ Ce-n-p Ba-d- γ (?) Ba ¹⁴⁰ β^- decay Ba >140 (6 min) β^- decay Ba >140 (18 min) β^- decay Th-n fission product Ba >140 (<1 min) β^- decay U-n fission product U-n(?)
	$\text{La} >140$	D		β^-	74 min			
	$\text{La} >140$	D		β^-	3.5 hr			
	$\text{La} >140$	E		β^-	<30 min			
	$\text{La} >140$	F		β^-	15 min			
	$\text{La} >140$	F		β^-	13 days			
58	Ce^{136}		<1		Stable			
	Ce^{138}		<1		Stable			
	Ce^{139}	F		β^+	2.1 min			Ce-n-2n(?)
	Ce^{140}		89		Stable			
	Ce^{140} *	B		IT, γ	140 days		0.21	La-d-n Ba- α -n

58	Ce ¹⁴¹	A		β^- , γ	28 days	0.5	0.22	Co-d-p Ce-n- γ Ce-n-2n Ba- α -n Pr-n-p U-n Ce-n- γ
	Ce ^{141, 143}	C			15 days	0.12		
	Ce ¹⁴²		11		Stable			
	Ce ¹⁴³	B(?)		β^-	33 hr	1.36	0.5	Co-d-p Ce-n- γ
	Ce ¹⁴⁴	B(?)		β^-	275 days	0.35		U-n (Xe parent)
	Ce	D		β^-	≤ 20 days			U-n (Xe parent)
	Ce	D		β^-	~ 15 min			U-n
	Ce	D		β^-	$\sim 4-5$ hr			U-n
	Ce	D		β^-	~ 40 hr			U-n
59	Pr ¹⁴⁰	A		β^+	3.5 min	2.40		Pr-n-2n
	Pr ¹⁴¹		100		Stable			
	Pr ¹⁴²	A		β^- , γ	19.3 hr	2.14	1.9	Pr-n- γ Nd-n-p Pr-d-p Ce-p-n La- α -n U-n
	Pr ¹⁴³	B		β^-	13.8 days	1.0		Ce ¹⁴³ β^- decay
	Pr	D		β^-	25 min			U-n Ce (~ 15 min) β^- decay

* Radioactive isomer of stable nucleus.

TABLE I (Continued)
 RADIOACTIVE AND STABLE ISOTOPES OF THE RARE EARTHS

Atomic Number <i>Z</i>	Isotope <i>A</i>	Class	Abundance %	Radiation	Half-Life, τ	Energy of Radiation, Mev		Formed by the Nuclear Reaction
						β	γ	
60	Nd ¹⁴¹	E		β^+	2.5 hr	0.78		Nd- <i>d</i> -H ³ (?) Nd- <i>n</i> -2 <i>n</i> Pr- <i>p</i> - <i>n</i> Nd- γ - <i>n</i>
	Nd ¹⁴²		25.95		Stable			
	Nd ¹⁴³		13.0		Stable			
	Nd ¹⁴⁴		22.6		Stable			
	Nd ¹⁴⁵		9.2		Stable			
	Nd ¹⁴⁶		16.5		Stable			
	Nd ^{147, 149}	E		β^-	47 hr	0.95		Nd- <i>d</i> - <i>p</i> Nd- <i>n</i> - γ Nd- <i>n</i> -2 <i>n</i> (?) U- <i>n</i>
	Nd ¹⁴⁷	(?)		β^-, γ	11 days	{ 0.4 } { 0.85 }	0.6	
	Nd ¹⁴⁸		6.8		Stable			
	Nd ¹⁵⁰		5.95		Stable			
61	Nd ¹⁵¹	E		β^-	21 min	0.2		Nd- <i>n</i> - γ U- <i>n</i>
	61 ¹⁴⁷	(?)		β^-	~4 yr			Nd- <i>d</i> - <i>n</i>
	61	F		β^-	12.5 hr		0.67	Pr- α - <i>n</i> Nd- <i>d</i> - <i>n</i>
	61	E		K or IT, γ	~200 days			Nd- <i>p</i> - <i>n</i> Nd- <i>d</i> - <i>n</i> Nd- α - <i>p</i>
	61	E		β^-, γ	5.3 days	2		
	61	E						

61	61	E		β^-, γ	2.7 hr	2	Nd- <i>p-n</i> Nd- <i>d-n</i> Nd- α - <i>p</i> Nd- <i>d-n</i>
62	61	E		β^-, γ	16 days	1.7	
	Sm ¹⁴⁴		3		Stable		
	Sm ¹⁴⁷		17		Stable		
	Sm ¹⁴⁸	A	14	α	1.4×10^{11} yr	2.0 (α)	Natural
	Sm ¹⁴⁹		15		Stable		
	Sm ¹⁵⁰		5		Stable		
	Sm ¹⁵²		26		Stable		
	Sm ¹⁵⁴		20		Stable		
	Sm	D		β^-	21 min	1.8	Sm- <i>n</i> - γ Sm- <i>n</i> -2 <i>n</i> (?) Sm- γ - <i>n</i> Sm- <i>d</i> - <i>p</i> Nd- α - <i>n</i> Sm- <i>n</i> - γ Sm- <i>n</i> -2 <i>n</i> (?) Sm- <i>d</i> - <i>p</i> Sm- γ - <i>n</i> Nd- α - <i>n</i> Sm- <i>d</i> - <i>p</i> Sm- <i>n</i> - γ Nd- α - <i>n</i> Sm- <i>n</i> - γ Nd- α - <i>n</i> Eu- <i>n</i> -2 <i>n</i> (?)
	Sm ¹⁵³			<i>IT</i>	46 hr	~ 0.6	
	Sm	E			60 days		
63	Eu ¹⁵⁰	E		β^+	27 hr		
	Eu ¹⁵¹		49.1		Stable		
	Eu ¹⁵²	B		$\beta^-, \gamma, e^-; K(?)$	9.2 hr	1.88 (β^-)	Eu- <i>n</i> - γ Eu- <i>n</i> -2 <i>n</i> (?) Eu- <i>d</i> - <i>p</i>
						0.123; 0.163; 0.725	

66	Dy ¹⁵⁸	0.1			Stable	
	Dy ¹⁶⁰	1.5			Stable	
	Dy ¹⁶¹	22			Stable	
	Dy ¹⁶²	24			Stable	
	Dy ¹⁶³	24			Stable	
	Dy ¹⁶⁴	28			Stable	
	Dy ¹⁶⁵	A	β^- , γ	1.20; 1.18; 1.1 1.40	Dy- n - γ	
67	Dy(?)	F	β^+	2.2 min	Dy- n -?	
	Ho ¹⁶⁴	F	β^-	47 min	Ho- n -2n(?)	
	Ho ¹⁶⁵	100		Stable		
68	Ho ¹⁶⁶	B	β^-	27 hr	Ho- n - γ	
	Er ¹⁶²	0.1		Stable		
	Er ¹⁶⁴	1.5		Stable		
	Er ¹⁶⁵	F	β^+	1.1 min	Er- n -2n(?)	
	Er ¹⁶⁶	32.9		Stable		
	Er ¹⁶⁷	24.4		Stable		
	Er ¹⁶⁸	26.9		Stable		
	Er ^{169, 171}	C		7 min	Er- n - γ	
	Er ^{169, 171}	C		12 hr	Er- n - γ	
69	Er ¹⁷⁰	14.2	β^-	Stable		
	Tm ¹⁶⁹	100		Stable		
70	Tm ¹⁷⁰	A		105 days	Tm- n - γ	
	Yb ¹⁶⁸	0.06		Stable		
	Yb ¹⁷⁰	4.21		Stable		
	Yb ¹⁷¹	14.26		Stable		

TABLE I (Continued)
 RADIOACTIVE AND STABLE ISOTOPES OF THE RARE EARTHS

Atomic Number Z	Isotope	Class	Abundance %	Radiation	Half-Life	Energy of Radiation, Mev		Formed by the Nuclear Reaction
						β	γ	
70	A							
	Yb ¹⁷²		21.49		Stable			Yb-n- γ
	Yb ¹⁷³		17.02		Stable			Yb-n- γ (?)
	Yb ¹⁷⁴		29.58		Stable			
	Yb ^{176, 177}	C			3.5 hr			
	Yb ¹⁷⁶		13.38		Stable			
71	Yb	G			41 hr			
	Lu ¹⁷⁵		97.5		Stable			
	Lu ¹⁷⁶	A	2.5	β^- , γ	7.3×10^{10} yr	0.215; 0.40	0.260	Natural
	Lu ¹⁷⁶	C		β^-	3.4 hr	1.150		Lu-n- γ
	Lu ¹⁷⁷	C		β^-	6.6 days	0.440		Lu-n- γ
	Th ²³²	A	100	α	1.39×10^{10} yr	4.20 (α)		Natural
92	U ²³⁴	A	0.006	α	2.69×10^5 yr	4.71; 4.78; 4.76 (α)		Pa ²³⁴ β^- decay
	U ²³⁵	A	0.71	α	7.7×10^8 yr	4.52 (α)		Natural
	U ²³⁷	A		β^- , γ	~ 7 days	0.26		U-n-2n
	U ²³⁸	A	99.28	α	4.51×10^9 yr	4.2 (α)		Natural
	U ²³⁹	A		β^-	23 min			U-n- γ
	Np ²³⁹	A		β^- , γ	2.3 days	0.47	0.22; 0.27	U ²³⁹ β^- decay
93								
94	Pu ²³⁹	A		α	2.4×10^4 yr			Np ²³⁹ β^- decay

In Table II are presented values for the absorption cross section of the rare earths (and some other representative elements) for thermal neutrons (neutron energy distribution corresponding to Maxwell distribution at room temperature) and for fast neutrons (one to several

TABLE II
NEUTRON ABSORPTION CROSS SECTIONS (IN BARNS)

Element	Atomic No.	Chief Process	Cross Section	
			Thermal	Fast
H	1	<i>S</i>	40	1.7
D	1	<i>S</i>	4.0	1.7
Li ⁶	3	α	900	1.8
Be	4	<i>S</i>	5.3	1.6
B ¹⁰	5	α	3,000	1.8
C	6	<i>S</i>	4.1	1.6
N	7	<i>S, p</i>	11.3	1.8
O	8	<i>S</i>	3.3	
Y	39		30	
Cd	48	<i>C</i>	2,600	
La	57		80	
Ce	58		~25	
Pr	59		25	
Nd	60		220	
Sm	62	<i>C</i>	4,300	
Eu	63		2,500	
Gd	64		30,000	
Tb	65		<1,000	
Dy	66		700	
Ho	67		100	
Er	68		120	
Tm	69		500	
Yb	70		90	
Lu	71		~400	
Th	90		32	
U	92		43	

Mev).* The chief process responsible for the experimentally observed absorption of thermal neutrons is shown, where known, by the following notation:

C = radiative capture.

S = elastic scattering.

p = proton emission.

α = alpha-particle emission.

* Taken from the table of Bethe, *Rev. Modern Phys.* 9, 69 (1937).

Usually, capture may be assumed to be the chief process if the cross section is large (more than 10 barns, if $Z > 10$), and scattering if the cross section is small. Scattering and disintegration processes are probable for fast neutron absorption. As Bethe (*loc. cit.*) points out, the cross sections for the rare earths may be in error owing to the presence of gadolinium, samarium, or europium in the samples.

Appendix 2

GENERAL PHYSICAL CONSTANTS

Table III contains chemically relevant values taken mainly from the 1941 list of the general (fundamental) physical constants. The 1941 list is due to Birge [*Rev. Modern Phys.*, **13**, 233 (1941)], who has given

TABLE III
GENERAL PHYSICAL CONSTANTS

Name	Symbol	Value
Velocity of light	c	2.99776×10^{10} cm/sec
Volume of ideal gas	V_0	22.4140 liters/mole
Ice point, 0°C	T_0	273.16°K
Faraday constant	F_0	96,501 international coulombs/ chem. equiv.
Electronic charge	e	4.8025×10^{-10} esu
Specific electronic charge	e/mc	1.7592×10^7 emu/g
Specific electronic charge	e/m	5.2736×10^{17} esu/g
Avogadro's number	N_0	6.0228×10^{23} mole $^{-1}$
Planck constant	h	6.6242×10^{-27} erg. sec
Boltzmann constant	k	1.38047×10^{-16} erg/deg
Gas constant	R_0	1.98670 cal/deg/mol
International ohm	p	1.00048 absolute ohms
International ampere	q	0.99986 absolute ampere
Calorie ¹	J	4.1833 international joules
Calorie ¹	J	4.1850 absolute joules
Standard gravitational acceleration	g	980.665 cm/sec ²
Standard density of mercury at 0°C	ρ_{Hg}	13.59504 g/cm ³
Liter	l	1000.028 cm ³
Bohr magneton	$\mu_0 = \frac{he}{4\pi mc}$	0.9273×10^{-20} erg/gauss
Bohr magneton	$\mu_0 N_0$	5585.2 ergs/gauss/mole
Atomic weight of electron	m	0.000545
Mass of atom of unit atomic weight	M_0	1.660×10^{-24} g
Energy associated with unit wave-number	E/ν	1.9627×10^{-16} erg cm
Energy of one-abs-volt-electron	...	1.6020×10^{-12} erg
Energy per mole, equivalent to 1-abs-volt-electron	...	23053 cal
Energy in Mev equivalent to unit atomic weight	...	932 Mev

¹ Chemists' defined calorie, now in common use.

TABLE IV
INTERNATIONAL CHEMICAL ATOMIC WEIGHTS *

	Sym- bol	Atomic Number	Atomic Weight		Sym- bol	Atomic Number	Atomic Weight
Aluminum...	Al	13	26.97	Molybdenum..	Mo	42	95.95
Antimony....	Sb	51	121.76	Neodymium..	Nd	60	144.27
Argon.....	A	18	39.944	Neon.....	Ne	10	20.183
Arsenic.....	As	33	74.91	Nickel.....	Ni	28	58.69
Barium.....	Ba	56	137.36	Nitrogen.....	N	7	14.008
Beryllium....	Be	4	9.02	Osmium.....	Os	76	190.2
Bismuth.....	Bi	83	209.00	Oxygen.....	O	8	16.0000
Boron.....	B	5	10.82	Palladium....	Pd	46	106.7
Bromine.....	Br	35	79.916	Phosphorus...	P	15	30.98
Cadmium.....	Cd	48	112.41	Platinum.....	Pt	78	195.23
Calcium.....	Ca	20	40.08	Potassium....	K	19	39.096
Carbon.....	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium.....	Ce	58	140.13	Protactinium..	Pa	91	231
Cesium.....	Cs	55	132.91	Radium.....	Ra	88	226.05
Chlorine.....	Cl	17	35.457	Radon.....	Rn	86	222
Chromium....	Cr	24	52.01	Rhenium.....	Re	75	186.31
Cobalt.....	Co	27	58.94	Rhodium.....	Rh	45	102.91
Columbium... Cb	41	92.91	Rubidium.....	Rb	37	85.48	
Copper.....	Cu	29	63.57	Ruthenium....	Ru	44	101.7
Dysprosium..	Dy	66	162.46	Samarium.....	Sm	62	150.43
Erbium.....	Er	68	167.2	Scandium....	Sc	21	45.10
Europium....	Eu	63	152.0	Selenium.....	Se	34	78.96
Fluorine....	F	9	19.00	Silicon.....	Si	14	28.06
Gadolinium..	Gd	64	156.9	Silver.....	Ag	47	107.880
Gallium.....	Ga	31	69.72	Sodium.....	Na	11	22.997
Germanium... Ge	32	72.60	Strontium....	Sr	38	87.63	
Gold.....	Au	79	197.2	Sulfur.....	S	16	32.06
Hafnium.....	Hf	72	178.6	Tantalum....	Ta	73	180.88
Helium.....	He	2	4.003	Tellurium....	Te	52	127.61
Holmium....	Ho	67	164.94	Terbium.....	Tb	65	159.2
Hydrogen....	H	1	1.0080	Thallium....	Tl	81	204.39
Indium.....	In	49	114.76	Thorium.....	Th	90	232.12
Iodine.....	I	53	126.92	Thulium.....	Tm	69	169.4
Iridium.....	Ir	77	193.1	Tin.....	Sn	50	118.70
Iron.....	Fe	26	55.85	Titanium.....	Ti	22	47.90
Krypton.....	Kr	36	83.7	Tungsten....	W	74	183.92
Lanthanum... La	57	138.92	Uranium.....	U	92	238.07	
Lead.....	Pb	82	207.21	Vanadium....	V	23	50.95
Lithium.....	Li	3	6.940	Xenon.....	Xe	54	131.3
Lutecium....	Lu	71	174.99	Ytterbium....	Yb	70	173.04
Magnesium... Mg	12	24.32	Yttrium.....	Y	39	88.92	
Manganese... Mn	25	54.93	Zinc.....	Zn	30	65.38	
Mercury.....	Hg	80	200.61	Zirconium....	Zr	40	91.22

* G. P. Baxter, *J. Am. Chem. Soc.*, **65**, 1443 (1943).

Because the basis for this table is 16.0000 for ordinary oxygen, the values are slightly different from those used and published by physicists. The basis for the physicists' tables is the isotope $O^{16} = 16.00000$; this refinement is essential when mass (energy) balances are being computed.

much careful attention to the values of the physical constants; there can be little doubt as to the current reliability of the values which he has published. [See also Benford, *Phys. Rev.*, **63**, 212 (1943); Birge, *Phys. Rev.*, **64**, 213 (1943)]. It will be understood that the values are subject to periodic revision.

Table V contains the atomic weights of some of the principal isotopes of the lighter elements on the basis of $O^{16} = 16.00000$.

TABLE V

ATOMIC MASSES OF STABLE ISOTOPES *

H ¹	1.00813	C ¹²	12.003892	Na ²³	22.0002	S ³⁴	33.9804
H ²	2.01473	C ¹³	13.00758	Mg ²⁴	23.9926	Cl ³⁵	34.9805
H ³	3.01705	N ¹⁴	14.007526	Mg ²⁵	24.9941	A ³⁶	35.9791
He ³	3.0170	N ¹⁵	15.00494	Mg ²⁶	25.9899	Cl ³⁷	36.9786
He ⁴	4.003842	O ¹⁶	16.00000	Al ²⁷	26.9902	A ³⁸	37.97544
Li ⁶	6.01687	O ¹⁷	17.00450	Si ²⁸	27.9870	K ³⁹	38.97518
Li ⁷	7.01811	O ¹⁸	18.00490	Si ²⁹	28.9865	A ⁴⁰	39.97504
Be ⁸	8.00792	F ¹⁹	19.00447	Si ³⁰	29.9834	Ca ⁴⁰	39.9745
Be ⁹	9.01505	Ne ²⁰	19.998926	P ³¹	30.9851	K ⁴¹	40.9739
B ¹⁰	10.01619	Ne ²¹	20.99980	S ³²	31.9823	Ca ⁴²	41.9711
B ¹¹	11.01290	Ne ²²	21.99862	S ³³	32.98260	Ca ⁴²	42.9723

Mass of neutron = 1.00895

* Hahn, Flüge, and Mattauch, *Physik. Z.*, **41**, 1 (1940).

Appendix 3

TABLE VI

THE PERIODIC SYSTEM OF THE ELEMENTS

I	I'	II	II'	III	III'	IV	IV'	V	V'	VI	VI'	VII	VII'	VIII	A	B	C
H 1														He 2			
Li 3		Be 4		B 5		C 6		N 7			O 8		F 9	Ne 10			
Na 11		Mg 12		Al 13		Si 14		P 15			S 16		Cl 17	A 18			
K 19		Ca 20		Sc 21		Ti 22		V 23		Cr 24		Mn 25			Fe 26		Ni 28
	Cu 29		Zn 30		Ga 31		Ge 32		As 33		Se 34		Br 35	Kr 36		Co 27	
Pb 87		Sr 38		Y 39		Zr 40		Cb 41		Mo 42					Ru 44		Pd 46
	Ag 47		Cd 48		In 49		Sn 50		Sb 51		Te 52		I 53	Xe 54		Rh 45	
Ce 58				La* 57		Hf 72		Ta 73		W 74		Re 75			Os 76		Pt 78
							Pb 82		Bi 83		Po 84					Ir 77	
— 87		Ra 88		Ac† 89										Rn 86			

* The rare-earth elements. (Lanthanide Series).
† The transcurium elements. (Actinide Series).
[For a discussion of these elements and the proposed names for the newly created 95 and 96 see Seaborg, Chem. and Eng. News, 29, 2190 (1946). The artificially formed elements are Np, neptunium; Pu, plutonium; (Am), americium; (Cm) curium.]

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